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HYDROESTERIFICATION OF 1-HEXENE

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Dedication

To my late Dad Mzwandile M'cLaren Mbuce.

Synopsis

Hydroesterification is the carbonylation of an olefin and the successive addition of an alcohol or water yielding an ester or acid. A variety of soluble palladium complexes are widely used for the hydroesterification of olefins due to their high activity and selectivity. Branched and linear carboxylic acid esters are formed in these reactions and the regioselectivity is strongly dependent on the catalytic system and reaction conditions used. For potential industrial applications, there is a need to understand the effect of catalyst and reaction parameters on the initial rate to enhance the yield of the desired isomer and to develop a suitable rate equation.

Standard carbonylation catalysts such as $Co_2(CO)_8$, $Fe(CO)_5$ and $Ni(CO)_4$ have been used to prepare fatty-acid esters. More recently, other catalysts based on Pd, Pt, Rh and Ru found widespread use because of their better performance under milder reaction conditions. Shell has intensively studied the use of palladium and ruthenium as halogen-free carbonylation catalysts. The palladium systems typically consist of palladium acetate, tertiary phosphines and strong acids such as mineral acids or acids with weak or non-coordinating anions such as sulfonic acids.

Although a number of reaction conditions have been reported for homogeneously catalysed transformations of olefins to esters, it has not been clear what the key intermediate of the Pd(II)-catalysed hydroesterification is. The proposals for the mechanism originate from the accepted cobalt-catalysed hydroformylation mechanism with modifications from the Heck formulations. Two mechanistic pathways have been proposed viz. the hydride mechanism and the alkoxy mechanism where the catalytic cycle starts from the insertion of the olefin into a Pd-H or a Pd-COOMe species respectively. It is well known that the active species could either be a hydride Pd-complex or an alkoxy Pd-complex (in the presence of an alcohol).

In this study, the kinetics of the hydroesterification of 1-hexene was investigated. The catalyst system used in this study was generated *in situ* from a mixture of $Pd(OAc)_2/PPh_3$/methanesulfonic acid. Reactions were carried out in a 100ml Hastelloy autoclave at 90°C and 70 bar carbon monoxide pressure. The performance of the *in-situ* generated, catalytic system was evaluated in terms of activity (turnover frequency, TOF) and the selectivity towards the various product compounds.

For these reactions, the TOF was constant in the initial 15 minutes whereupon it decreased significantly. The following reaction and catalyst variables were studied: 1-hexene concentration, carbon monoxide pressure, methanol concentration, temperature; palladium, ligand and acid concentrations.

The reaction rate was approximated to be first-order with respect to 1-hexene concentration. An increase in the carbon monoxide above 10 bar and palladium concentration strongly inhibited the hydroesterification of 1-hexene. On varying the methanol concentration, the TOF passed a pronounced maximum at ca. 7.7 mol/litre. The reaction became inhibited by methanol at high methanol concentrations. A similar trend was observed for the selectivity for the formation of esters, which passed a maximum at ca. 10 mol/litre.

The molar ratio of triphenylphosphine to palladium showed a significant influence in the catalyst activity and product selectivity. The TOF passed a maximum at an excess of 30 indicating the need for a large excess of the ligand for the formation of the catalytically active complex. The selectivity for ester formation also passed a maximum with increasing ligand concentration. The presence of an acid was found to be necessary to form the catalytically active cationic species.

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List of Symbols

Symbol	Description	Units
TOF	Turnover frequency	$mol.mol^{-1}.hr^{-1}$
$n_{CO,consumed}$	Number of moles of CO consumed	mol
n_{Pd}	Number of moles of palladium	mol
$V_{ballast}$	Volume of the ballast vessel	litre
R_f	Response factor	-
X	Conversion of 1-hexene	%
S_P	Selectivity to compound P	%
$C_{n\text{-}ester}$	Content of methylheptanoate in the fraction of esters	%
$n_{totalesters}$	Number of moles of C8-esters	mol
r_{DB}	Rate of double-bond isomerisation	$mol.mol^{-1}.hr^{-1}$
$-r_{CO}$	Rate of CO consumption	$mol.mol^{-1}.hr^{-1}$

Glossary

CG	Carrier gas
CO	Carbon monoxide
GC	Gas Chromatograph/y
GC-MS	Gas-Chromatograph – Mass Spectroscopy
MSA	Methanesulfonic acid
p-TSA	para-Toluenesulfonic acid
PPh_3	Triphenylphosphine
PR_1	Diphenyl-2-pyridylphosphine
PR_2	Tris(p-methoxyphenyl)phosphine
PBu_3	Tributylphosphine
$P(OPh)_3$	Triphenylphosphite

1. LITERATURE REVIEW

1.1 Introduction

A key point of homogeneous organometallic catalysis was established when Otto Roelen passed a mixture of ethylene and synthesis gas over a fixed-bed cobalt-containing catalyst at 150°C and 100 bar pressure [1]. It must be attributed to Roelen's experimental expertise that he detected, isolated and characterised the small amounts of propanal (and diethyl ketone) that had formed under these unconventional Fischer-Tropsch conditions. His clear scientific awareness enabled him to draw the right conclusions from the unexpected experimental results viz. the formation of aldehydes from olefins and synthesis gas. However, it took some time until the general principles and the broad applicability of metal-carbonyl-catalysed reactions were fully recognized and the homogeneous nature of the catalysis was proven.

25 years after the initial search into carbonylation, it was found that reactions still required the use of high temperatures (100-300°C) and pressures (100-1000 bar), expensive autoclave equipment, large quantities of dangerously toxic, volatile and unstable catalysts [$Ni(CO)_4$, $Fe(CO)_5$ and $HCo(CO)_4$] [2d]. Usually a complex mixture of products was obtained, which required separation. Consequently, carbonylation was scarcely to be contemplated as a basis for fine-chemical production and a laboratory-scale research tool.

Dramatic changes featured in the second 25 years with the work of Wilkinson [2a], Heck [2b] and Tsuji [2c] which led to the discovery of stable but extremely active catalysts based on organophosphine complexes of rhodium and palladium. As a result, many carbonylation reactions can now be conducted at low temperatures (below 100 ^{0}C), at pressures close to atmospheric pressure and using small quantities (0.1 to 1 mole% on the basis of the substrate) of involatile, air-stable catalyst precursors such as $Pd(PPh_3)_2Cl_2$ which are converted *in situ* to the active species [2d].

The exothermic reaction (ΔH = -65.4 kJ/mol) of ethylene with carbon monoxide in the presence of water to produce propionic acid is an example of an industrially operating carbonylation reaction [3]. In 1943, nickel chloride was patented as the catalyst for this reaction. However, for the industrial-scale process, a halogen-free system is used. Propionic acid is formed according to the following reaction [4] :

$$CH_2{=}CH_2 + CO + H_2O \xrightarrow{Ni(CO)_4} CH_3CH_2COOH \qquad \textbf{(1.1)}$$

The catalyst is generated under reaction conditions from nickel(II) salts. The mechanism of this process has not been fully established but it has been suggested that $Ni(CO)_4$ which is formed *in situ* using one molecule of carbon monoxide as a reducing equivalent is protonated yielding the active catalyst [5] (See Figure 1.1).

$$NiX_2 + 5CO + H_2O \longrightarrow Ni(CO)_4 + CO_2 + 2HX$$

$$Ni(CO)_4 + HX \longrightarrow HXNi(CO)_2 + 2CO$$

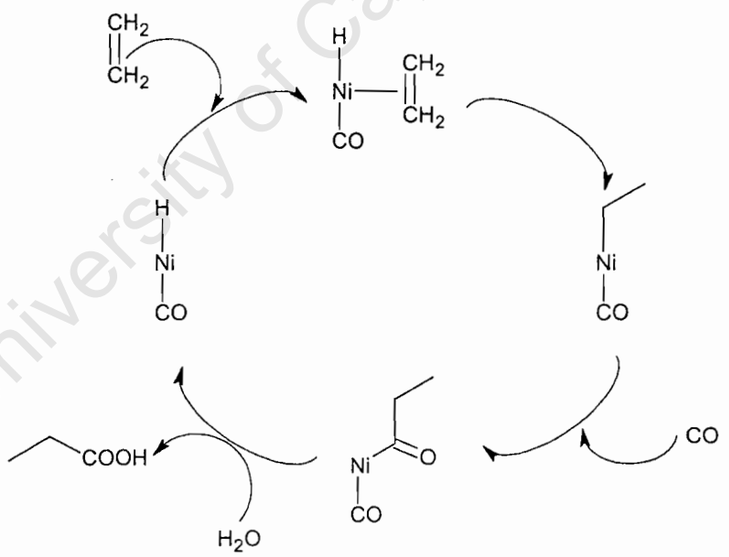


Figure 1.1 : Catalytic cycle of the carbonylation of ethene with nickel [5].

The catalyst used is a nickel hydride complex that is generated under the reaction conditions (250-320°C and 100-300 bar) by reduction of the nickel salt. $Ni(CO)_4$ is a precursor to the active species [4]. Assuming the catalyst to be a nickel hydride complex, the mechanism for the formation of propionic acid follows the elementary steps of the catalytic cycle as shown in Figure 1.1. Addition of ethene to the hydride intermediate generates a complex which after insertion of CO and nucleophilic attack of water, releases propionic acid with regeneration of the initial hydride intermediate.

The industrial-scale BASF process is characterized by low raw material costs, high conversion and yield, and a simple work-up [14] (See Figure 1.2). Ethylene and carbon monoxide are compressed and continuously pumped into the high-pressure reactor **1** together with the feed solution. The crude propionic acid formed at 100-300 bar and 250-320°C is drawn off at the top of the reactor and cooled in a heat exchanger **2**, generating steam. Part of the cooled crude propionic acid is recycled to the reactor for temperature regulation **3**. The main quantity is allowed to expand and is separated into an off-gas and a crude acid stream **4**.

Nickel is recovered from the off-gas and recycled to the reactor. The off-gas is incinerated with recovery of heat. The crude acid stream is subsequently dehydrated and worked up by distillation in several columns **5**. The nickel salts thus formed are recycled to the process. The pure propionic acid is finally obtained by distillation. The product residue is channelled out of the process [14]. Due to its corrosiveness, which is not only determined by the water content, pressure and temperature, but also by the degree of purity, ordinary steel is not suitable for handling propionic acid. Only silver has proved to be a suitable reactor material [6].

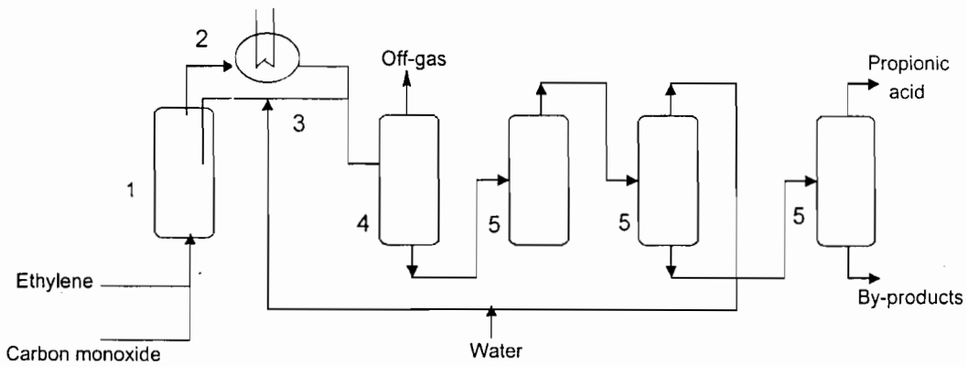


Figure 1.2 : BASF process for the production of propionic acid [14]

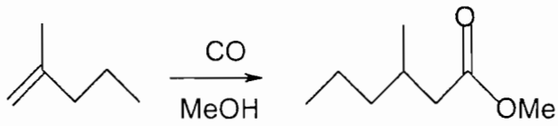
Shell has intensively studied the use of palladium and ruthenium as halogen-free carbonylation catalysts [7]. The catalysts were principally designed for the carbonylation of olefins in the presence of alcohols to yield carboxylic esters but also work well for the synthesis of carboxylic acids and anhydrides. The palladium systems typically consist of palladium acetate, tertiary phosphines and strong acids such as mineral acids or acids with weak or noncoordinating anions such as sulfonic acids. Remarkable activities have been reported when aromatic phosphines that carry pyridines as substituents are used [8]. The reaction conditions that are required with ruthenium as the active metal centre are more severe than similar palladium systems.

The hydroesterification is catalysed by a variety of transition metal complexes including $Co_2(CO)_8$, H_2PtCl_6 and $Pd(PPh_3)_2$ [9a]. However, it has been reported [9a] that hydroesterification of 1-alkenes at 80°C and 200 bar in the presence of ligand-stabilised bimetallic catalysts based on tin(II)chloride and either platinum or palladium complexes yields linear products with up to 98% selectivity. It was also shown that, with platinum-based catalysts, selectivity for linear ester formation increases with alkene chain length and the reaction rate reaches a maximum around C_7.

Slightly higher selectivity for branched-chain esters was observed with palladium-based catalysts derived from $Pd(PPh_3)_2Cl_2$ and $SnCl_2$ [9a]. The palladium systems have a commercial potential over other transition metal

complexes because they are effective at lower pressures. The palladium systems have greater flexibility with respect to the structure of substrate and significantly lower cost. It has been reported that the presence of alkyl groups adjacent to the double bond in 1-alkenes can greatly enhance the selectivity for linear products e.g. hydroesterification of 2-methyl-1-pentene gives 3-methylhexanoate with >99% selectivity at 30% conversion [9a].

Reaction:



(1.2)

Looking at the potential application of olefin carboxylation in industry, there is a need to understand the effect of catalyst and reaction parameters on the initial rate to enhance the yield of the desired isomer and to develop a suitable rate equation. A variety of soluble palladium complexes are widely used for transition metal catalysed hydroesterification of olefins due to their high activity and selectivity [2]. Branched and linear carboxylic acid esters are formed in these reactions and the regioselectivity is strongly dependent on the catalytic system and reaction conditions used [34, 35].

It is widely reported that in the presence of water and alcohol, palladium complexes catalyse the reaction of an olefin with carbon monoxide to give carboxylic acids and esters respectively [2]. In recent years, palladium complexes containing phosphine ligands have attracted a lot of interest both in academic and industrial studies. The phosphine ligands are weakly coordinating to the palladium yielding a metal cation with easily available coordination sites capable of activating the reactant molecules [17-20].

1.2 Utility of esters

Organic esters are widely used as plasticisers in polymers [9b]. They soften and make inherently rigid and even brittle polymers more flexible. Unsaturated and difunctional esters are important monomers for the manufacture of many polymers in commercial use e.g. methyl methacrylate is the monomer for poly(methyl methacrylate). Esters are important fragrance and flavour compounds used in the production of perfumes, flavours, cosmetics, soaps, detergents and air-fresheners. Higher esters are non-ionic surfactants used in food, pharmaceuticals, cosmetics and other applications.

1.3. Catalysis

Standard carbonylation catalysts such as $Co_2(CO)_8$ and $Ni(CO)_4$ have been used to prepare fatty-acid esters [13]. More recently, other catalysts based on Pd, Pt, Rh and Ru found widespread use because of their better performance under milder reaction conditions [2]. As seen in Table 3.3, hydrocarboxylation of simple olefins with palladium catalysts occurs at temperatures of 70-120°C and 1-150 bar, while cobalt catalysts needed 150-200°C and 130-200 bar [14].

Table 1.1 : Comparison of hydrocarboxylations with different catalysts [14]

Catalyst	$Co_2(CO)_8$	$Ni(CO)_4$	PdX_2L_2	$PtX_2L_2 + SnX_2$	RhX_3
Temp, °C	150-200	200-320	70-120	80-100	100-130
Pressure, bar	130-200	150-300	1-150	1-200	1-100

Palladium is one of the most versatile and efficient catalyst metals in organometallic synthesis, be it in elemental forms or as palladium salts and complexes [14]. Both the renaissance of organometallic chemistry in the 1960s and the subsequent breakthrough of homogeneous organometallic catalysis in laboratory scale and industrial syntheses have received a major stimulus from palladium coordination chemistry. Platinum catalysts are superior concerning the regioselectivity of ester formation, especially with tin compounds as co-catalysts. However, the rates remain quite low even under high pressure.

Among the basic types of palladium-catalysed transformations, the Heck reaction and related chemistry occupy a special place. In the Heck process the catalyst is often anything containing palladium [15]. Other metals such as ruthenium can perform the task in the absence of palladium. Palladium complexes with or without the phosphine ligands can catalyse the reaction. A primary role of the phosphine ligands is to support palladium in its zero oxidation state in the form of PdL_4 or PdL_3 species. The phosphine-assisted

method is the classical and well-established method which gives excellent results as it does not rely on an unknown reactivity of the catalyst species in a given cycle but rather on the ligands which can sustain the catalytically active species even outside of the catalytic cycle [15].

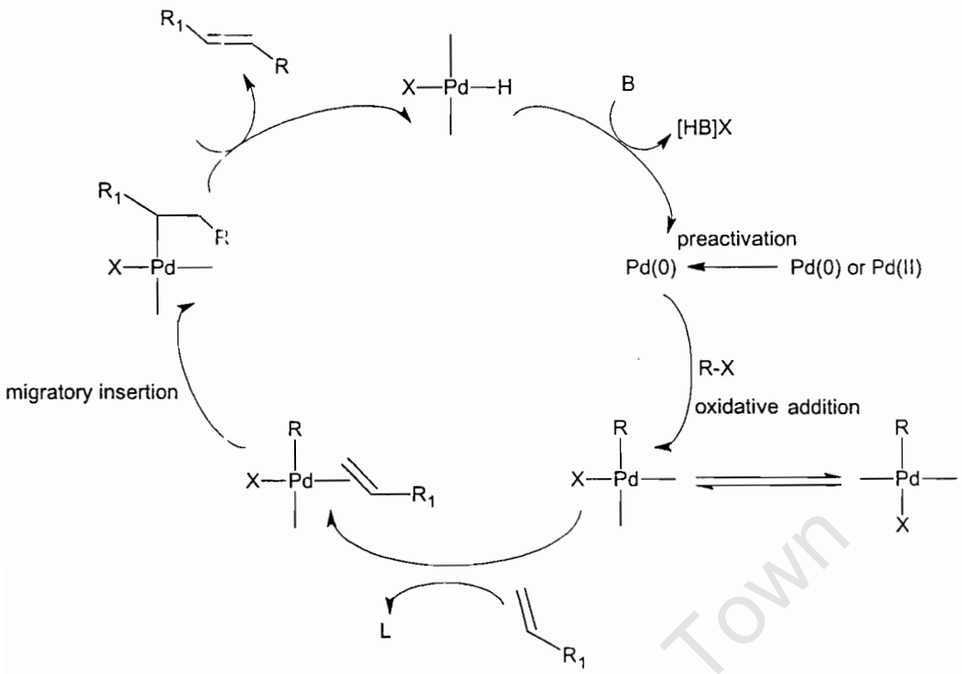


Figure 1.3 : A simplified version of the Heck catalytic cycle [15]

The entry into the catalytic cycle includes the reduction of Pd(II) complexes to Pd(0). The primary reduction of Pd(II) complexes to Pd(0) is mostly accomplished by phosphine in phosphine-modified catalytic cycles [16]. The reduction is assisted by hard nucleophiles like hydroxide and water. The Pd(0) species must have a proper coordination shell. Not more than two strongly bound ligands are allowed as illustrated in the catalytic cycle above. This requirement places a serious restriction on the choice of ligands and their concentration in the reaction mixture [15].

The reactivity of Pd(0) complexes is dominated by two features : Ease of dissociation and ease of oxidation [17]. In solution, the complexes dissociate according to the equilibria

$$PdL_4 \rightleftharpoons PdL_3 + L$$
$$PdL_3 \rightleftharpoons PdL_2 + L \qquad \textbf{(1.3)}$$

The most important problem of monodentate phosphine-based catalysis is the very low concentration of the reactive dicoordinated Pd(0) complex due to low equilibrium constants for the above reactions [15]. In the presence of excess ligand, the concentration of active species is strongly decreased which leads to inhibition of the catalytic process. Taking 2 equivalents of the ligand, the disproportionation of the dicoordinated complex to a stable tricoordinate complex and unstable low-ligated complexes occurs which undergo a fast aggregation to clusters and further to give off inactive metallic particles (Pd-black).

$$2PdL_2 \rightleftharpoons PdL_3 + PdL$$
$$PdL + PdL_2 \rightleftharpoons PdL_3 + \text{Pd-black} \qquad \textbf{(1.4)}$$

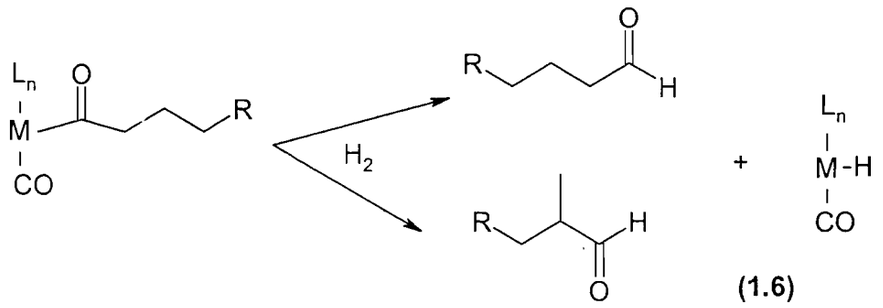
This problem arises in all methods of the generation of catalytically active palladium complexes even by a reaction of $Pd(OAc)_2$ with 3 equivalents of phosphine [15].

$$Pd(OAc)_2 + 3PPh_3 \longrightarrow Pd(PPh_3)_2 + Ph_3P{=}O \qquad \textbf{(1.5)}$$

The reaction of the product of oxidative addition with an olefin often requires that palladium loses one of the strongly bounded ligands to free a coordination site for the alkene [15]. In a carbonylation reaction with propylene, though significant amounts of Pd-black were obtained, two complexes were isolated $[PdCl(COOMe)(PPh_3)_2]$ and $[PdCl(COPr)(PPh_3)_2]$ [19]. The authors concluded that a Pd-H species is involved and that a

PdCOOMe species does not occur in the catalytic cycle implying olefin insertion occurring before CO-insertion. The origin of the Pd-H species could only be linked to the Heck oxidative addition of the alcohol.

In the hydroformylation process, the last step



(1.6)

is an irreversible process thus the linear and branched products do not come to equilibrium hence the kinetic ratio of the products is retained [12]. It is argued that 'it is not so much the regiochemistry of alkene insertion that decides this ratio but the rate at which primary and secondary alkyls are trapped by migration of CO'[11,12]. A commercially important discovery that the addition of phosphines gives a catalyst that is not only much more active but which also favours the primary over secondary aldehyde has been made. This is due to the steric bulk of the phosphine which encourages the formation of the less hindered species and speeds up migratory insertion.

In the hydroesterification of fluoro-olefins with methanol and CO at 100°C and 10 atm, catalytic effects of typical transition metal complexes such as $Co_2(CO)_8$, $Rh_6(CO)_{16}$, $H_2PtCl_6/SnCl_2$ and $PdCl_2(PPh_3)_2$ were investigated [10]. It was found that only $PdCl_2(PPh_3)_2$ showed catalytic activity high enough to promote the reaction at the investigated reaction conditions. Thus the authors decided to employ palladium complexes with phosphine ligands for the study.

Reaction:

$$RCH{=}CH_2 + CO + R^1OH \xrightarrow{[Pd]} \underset{\mathbf{1}}{RCH_2CH_2COOR^1} + \underset{\mathbf{2}}{R\text{-}(CH_3)\text{-}CHCOOR^1}$$

$$R = CF_3,\ C_6F_5 \qquad \textbf{(1.7)}$$

Hydroesterification of styrene with neutral palladium complexes such as $PdCl_2(PPh_3)_2$, $PdCl_2$(diphenylphosphino propane) was reported to proceed under severe conditions (200-700 atm of CO) and the activity was found to be rather low [36,37] Under these conditions, regioselective formation of the iso ester **2** was observed with monophosphines [36] as ligands and that of the normal ester **1** was observed with bidentate ligands [37].

Increased regioselectivity to the iso ester **2** was reported with $Pd(OAc)_2$ immobilised on montmorrilonite in the presence of HCl as a promoter under milder conditions of 25^0C and 600 psig of CO [38]. A similar homogeneous catalytic system comprising of $Pd(OAc)_2$ and diphenylphosphino acetic acid and p-toluenesulfonic acid was reported to have a drastic decrease in the regioselectivity (95%) to the iso ester **2** [39].

In recent developments, cationic palladium complexes with improved catalytic activity at milder reaction conditions have been reported [24,40-42]. It was shown that high selectivity to the branched ester **2** can be obtained if $Pd(OAc)_2$ catalyst is used along with PPh_3 and p-toluenesulfonic acid as promoter [40]. The *in situ* generated catalyst precursor $Pd(PPh_3)_2(OTs)_2$ has been successfully employed in the carbonylation of ethylene [37], styrene [24,43] and cyclohexene [42]. The weakly coordinating property of the TsO^- anion is believed to facilitate activation of substrate molecules [40-43].

The addition of PPh_3 ligand eliminates precipitation of the Pd metal [32]. However, at low concentrations of p-toluenesulfonic acid, the starting precursor $Pd(PPh_3)_2(TsO)_2$ is reduced to the inactive Pd(0) complex $Pd(CO)(PPh_3)_3$ or $[Pd(CO)(PPh_3)_3]_n$ probably via reactions 1.8 and 1.9 below as shown by the Infra-Red (IR) spectra of the solid recovered after the catalysis is attempted [44].

$$Pd(PPh_3)_2(TsO)_2 + CH_3OH + PPh_3 + CO \rightleftharpoons Pd(PPh_3)_3(CO) + HCHO + 2TsOH \quad \textbf{(1.8)}$$

$$Pd(CO)(PPh_3)_3 \overset{-PPh_3}{\rightleftharpoons} Pd(CO)(PPh_3)_2 \overset{+PPh_3}{\rightleftharpoons} [Pd(CO)(PPh_3)]_n \quad \textbf{(1.9)}$$

These polynuclear complexes are precursors to palladium-black. They can be reactivated by addition of TsOH, probably through formation of Pd-hydride species as illustrated in reaction 1.10 below [32].

$$Pd(PPh_3)_3(CO) + TsOH \rightleftharpoons [HPd(CO)(PPh_3)_2]^+TsO^+ + PPh_3 \quad \textbf{(1.10)}$$

1.4 Mechanisms

Although a number of reaction conditions have been reported for homogeneously catalysed transformations of olefins to esters, it has not been clear what the key intermediate of the Pd(II)-catalysed hydroesterification is. Much attention has been focused on the mechanism. The proposals for the mechanism originate from the accepted cobalt-catalysed hydroformylation mechanism with modifications from the Heck formulations as illustrated in Fig. 1.4 [20].

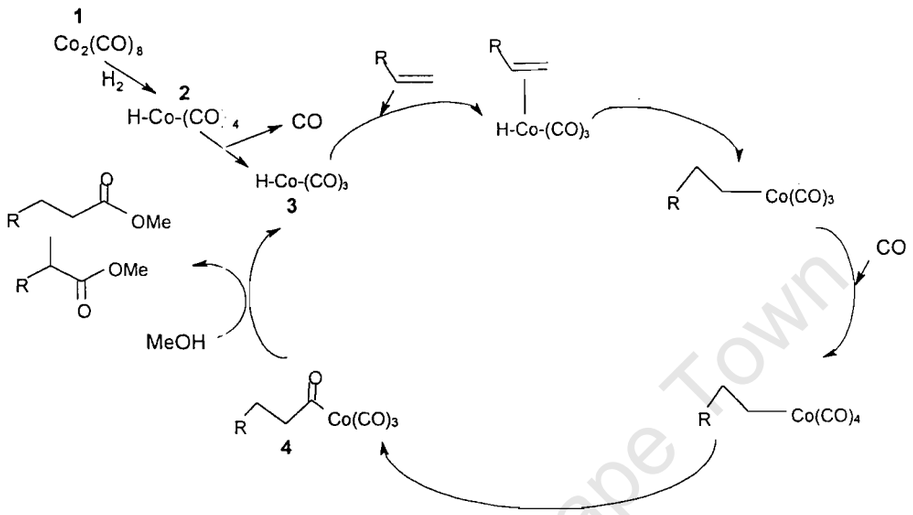
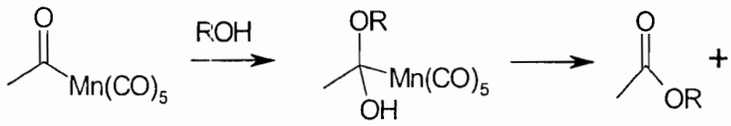


Figure 1.4 : Cobalt-catalysed carbonylation mechanism [20]

The reaction of compound **1** with H_2 or an alcohol forms $HCo(CO)_4$. This 'hydride' is actually a strong acid and quite unstable. It readily decomposes to Co metal in a CO- free atmosphere. High pressures are generally required in Co-catalysed reactions to stabilise $HCo(CO)_4$ and the intermediates in the cycle. It is commonly assumed that the catalytic cycle is entered by dissociation of a CO ligand to give $HCo(CO)_3$. Co-ordination and insertion of the olefin into the Co-H bond takes place. The subsequent steps are coordination and insertion of CO into the Co-olefin bond to give the labile acyl compound **4**. These steps are common to carboxylation and hydroformylation reactions. The difference lies in the mode of cleavage of the acyl group from

the metal. The acyl cleavage with an alcohol or water proceeds as shown in the cycle. The detailed mechanism for this step is not established but studies on the most stable manganese carbonyl derivative are suggestive where the initial reaction seems to involve the acid/ base catalysed addition of the -OH bond to the acyl carbonyl function [20].



(1.11)

Based on the Heck formulation and the proven involvement of $HPdCl(PPh_3)_2$ as the active species in palladium-catalysed hydroesterifications where isolation of *trans*-Pd-(COPr)$Cl(PPh_3)_2$ from propene hydroformylation [21] while $Pd(CO)(PPh_3)_2$ is inactive as a catalyst in the absence of HCl [22], the following mechanisms have been proposed for palladium-catalysed hydroesterification reactions. With PdX_2L_2/SnX_2 catalyst systems, olefins seem to be the hydrogen source for the formation of the active Pd-H species [23].

The mechanism of palladium-catalysed carbonylation is less well-defined. Two mechanistic pathways have been proposed:

1.4.1 The hydride mechanism [32]

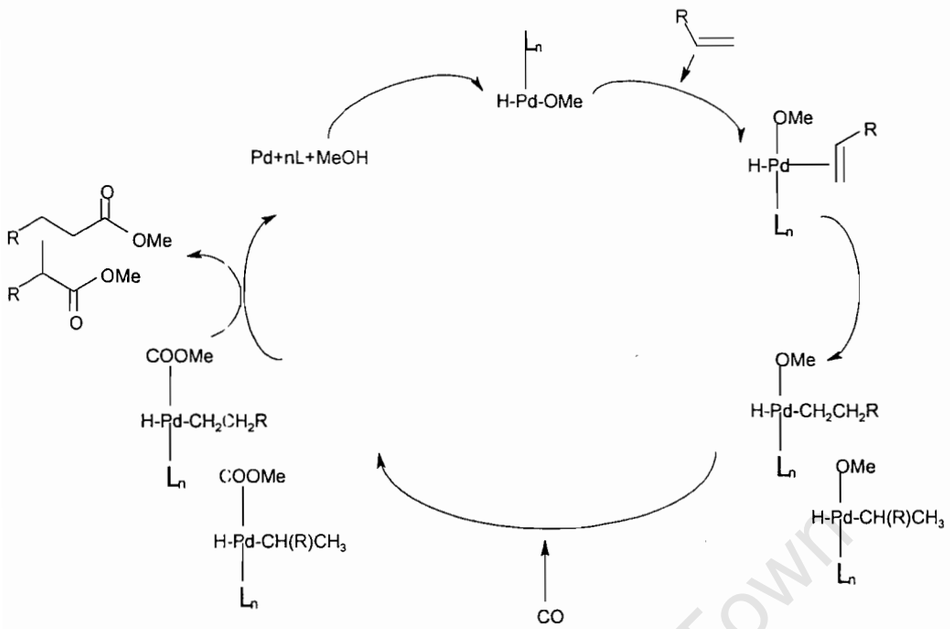


Figure 1.5 : The hydride mechanism [32]

By oxidative addition palladium reacts with the ligands to furnish the labile methoxy compound [32]. Insertion of the olefin to the complex gives rise to two products depending on whether the hydrogen migrates to the less or more substituted olefin-carbon. Co-ordination and insertion of CO into the Pd-O bond forms the crowded Pd complex. Cleavage of the Pd-C bond yields the ester and regenerates the Pd complex hence the Pd and ligands.

1.4.2 The alkoxy mechanism [32]

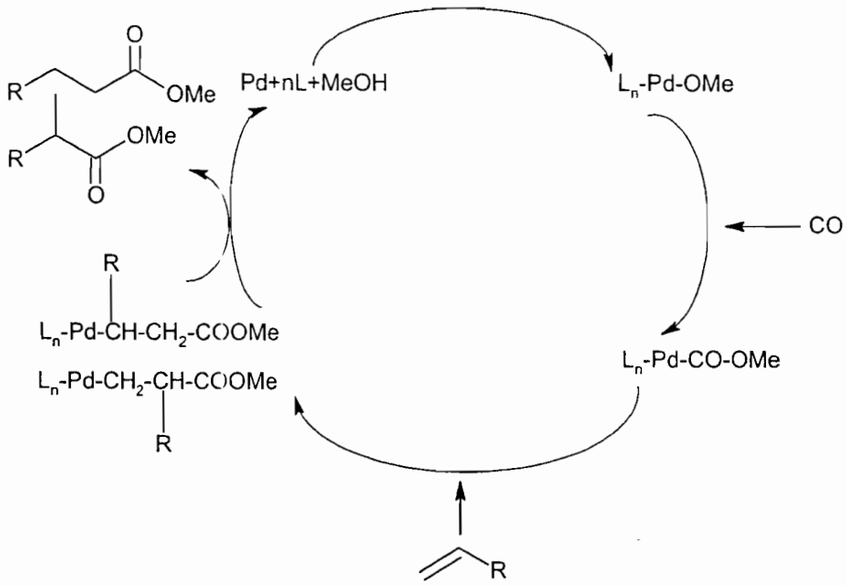


Figure 1.6 : The alkoxy mechanism [32]

The alkoxy mechanism is initiated by the insertion of an olefin into a palladium-carboalkoxy bond [32]. It is very likely that both pathways occur simultaneously since formation of palladium-methoxy complexes is quite facile in methanol as a solvent and that of palladium-hydride is favoured by the presence of acidic promoters.

Generally, nucleophilic attack of methanol to Pd-acyl complexes is regarded as the rate-determining step in the case of carbonylation of olefins proceeding through the Pd-H mechanism [32]. Hence to isolate the palladium-acyl species, the hydroesterification has to be carried out at lower temperatures (ca. 55 °C) where reaction rates are very low.

In carboxylations of olefins using palladium complex catalysts, it is well known that the active species could either be a hydride Pd-complex or an alkoxy Pd-complex (in the presence of an alcohol) [32]. The enhancement of reaction rate with water [41], p-toluenesulfonic acid and hydrogen [32] suggests that the hydroesterification reaction is likely to proceed through the hydride

mechanism. It was shown that in methanol as solvent, the alkoxy Pd-complex which is inactive or lower in activity is predominant [44]. With the homogeneous $Pd(OAc)_2/PPh_3$/p-toluenesulfonic acid catalyst system, it was proposed that the reaction proceeds through the hydride pathway and the active species is of the type $[HPd(PPh_3)_{n-z}(CO)]^+OTs^-$ [41]. The alkoxy and hydride species can form from the initially formed $Pd(OAc)_2(PPh_3)_2$. It was concluded that under the conditions, the fraction of palladium that forms the active species would depend mainly on the methanol concentration.

1.5 Reaction parameters

Kinetic studies in the hydroformylation reaction showed that the rate of aldehyde formation depended directly on the olefin, hydrogen and cobalt concentrations but inversely on the carbon monoxide concentration above 10 bar, where the reaction is normally carried out [20].

$$\frac{d[aldehyde]}{dt} = k \cdot \frac{[olefin] \cdot [Co] \cdot p_{H_2}}{p_{CO}} \qquad \textbf{(1.12)}$$

In contrast, at low CO partial pressures (<10 bar) an increasing concentration of carbon monoxide enhances the overall rate [14]. This reflects the necessity for carbon monoxide to generate the 16 electron $HCo(CO)_3$. At higher CO partial pressures, the less reactive $HCo(CO)_4$ is formed (see Fig. 1.4), therefore explaining the negative order of reaction at pCO > 10 bar.

Thus an industrially desirable high rate of aldehyde formation can be achieved in three ways [14]:
Low carbon monoxide partial pressure
High olefin and cobalt concentrations
High hydrogen partial pressure.

The carbon monoxide inhibition of the reaction arises because the reactive forms of the intermediates are coordinatively unsaturated and carbon monoxide competes with the other reactants for the available coordination sites [25]. It was shown that addition of $HCo(CO)_4$ to 1-pentene was inhibited by as little as 1 bar of carbon monoxide indicating that $HCo(CO)_3$ is the actual reactant.

$$[HCo(CO)_3] + CH_2{=}CH_2 \rightleftharpoons [CH_3CH_2Co(CO)_3]$$

$$[CH_3CH_2Co(CO)_3] + CO \rightleftharpoons [CH_3CH_2Co(CO)_4]$$

$$[CH_3CH_2Co(CO)_4] \rightleftharpoons [CH_3CH_2COCo(CO)_3]$$

$$[CH_3CH_2COCo(CO)_3] + CO \rightleftharpoons [CH_3CH_2COCo(CO)_4]$$

$$[CH_3CH_2COCo(CO)_3] + H_2 \rightleftharpoons [CH_3CH_2C(H)Co(CO)_3H]$$

$$[CH_3CH_2C(H)Co(CO)_3H] \longrightarrow CH_3CH_2CHO + [HCo(CO)_3] \qquad \textbf{(1.13)}$$

Presumably olefin coordination with the hydride is necessary before addition can occur [25]. The dissociated carbon monoxide then must reassociate and form the tetracarbonylalkylcobalt intermediates (eq. 1.13). A shift of the alkyl to a coordinated carbonyl produces an unsaturated tricarbonylacylcobalt(I) complex. Carbon monoxide now competes with hydrogen for this unsaturated species.

If the tetracarbonylacyl species is formed, it apparently cannot be reduced until it dissociates again since small amounts of carbon monoxide greatly decrease the rate of reduction of isolated tetracarbonylacylcobalt(I) complexes with hydrogen [25]. The hydrogen probably reduces the tricarbonylacyl complex by first oxidatively adding to the cobalt and then one hydrogen shifts from cobalt to the acyl carbon, a reaction which also regenerates the active catalyst $HCo(CO)_3$.

Another source of CO inhibition exists in the catalyst formation reaction.

$$Co_2(CO)_8 \rightleftharpoons Co_2(CO)_7 + CO$$

$$Co_2(CO)_7 + H_2 \rightleftharpoons [HCo(CO)_3] + [HCo(CO)_4]$$

$$[HCo(CO)_3] + CO \rightleftharpoons [HCo(CO)_4] \qquad \textbf{(1.14)}$$

Hydridotetracarbonylcobalt(I) readily loses hydrogen to form the octacarbonyldicobalt(0) species [25]. The reverse reaction is inhibited by CO (see eq. 1.14). Which of the possible sources is important depends on reaction conditions, reagent concentrations and olefin structure. With respect to conversion, selectivity and operation, the hydroformylation is influenced by a number of parameters. By fine-tuning of the operation conditions, a broad band of product compositions is achievable [14].

Kinetics of the hydroesterification of styrene were studied using $Pd(OAc)_2$, PPh_3 and p-toluenesulfonic acid as the catalyst system in methanol as solvent [41]. The reaction was found to be first order with respect to catalyst concentration and zero order with styrene up to a concentration of 3.84 kmol/m^3. At high concentrations of styrene (up to 6.73 kmol/m^3), a significant increase in the rate and formation of the iso product were observed. Kinetics of the hydroesterification of cyclohexene using preformed $Pd(PPh_3)_2(TsO)_2$ as catalyst in methanol as solvent were also studied. The initial reaction rate was found to increase linearly with the concentration of cyclohexene and methanol and passes through a maximum with increasing pressure of CO [42].

1.5.1 Temperature

The phosphine-modified cobalt catalyst introduced by Shell in 1966 led to an increase in selectivity towards linear products, an increase in thermal stability and hydrogenation activity but to a lower reactivity compared to the cobalt carbonyl catalyst systems [14]. In order to compensate for the lower activity, reaction temperatures had to be kept at about 180°C. With higher temperatures, n/i selectivity drops [26] as less coordinated cobalt species are

involved in the catalytic cycle. The reduced steric demand around the metal centre leads to increased formation of branched products. The decrease of the n/i ratio at higher temperatures is even more pronounced with modified rhodium catalysts [14]. Modern rhodium oxo plants are operating at temperatures of 120 °C to maintain a high n/i distribution.

In the hydroesterification of styrene in the range 338-358K, the n/i ratio was found to increase with an increase in temperature [41]. In the carbonylation of cyclohexene, the TOF increased up to 850 hr^{-1} on increasing the temperature to 373K [42].

1.5.2 Pressure

For ligand-modified catalysts (M = CO, Rh), the following general equilibrium is formulated [14] :

$$HM(CO)_x + y\ PR_3 \rightleftharpoons HM(CO)_{x-y}(PR_3)_y + y\ CO \qquad \textbf{(1.15)}$$

At low CO partial pressures, equilibrium is shifted to the right-hand side [14]. By coordination of ligands the metal centre becomes more sterically congested thus enhancing formation of linear products. With increasing CO partial pressure the n/i ratio diminishes constantly. Only at higher pressures is the catalytic cycle dominated by $HM(CO)_4$ species thus favouring linear products again.

In the hydroesterification of styrene, an increase in the pressure of CO enhanced the selectivity to the iso product [14] .The possible reason may be an increase in the formation of a dicarbonylpalladium species thus favouring formation of a Pd species having styrene in the iso coordination. The rate of reaction increasec with an increase in the partial pressure of CO initially and was independent beyond 3.5 MPa [41]. With the cyclohexene, the initial rate passed through a maximum at 3.5 MPa followed by a steady decline on increasing the partial pressure of CO [42].

1.5.3 Catalyst concentration

A general rule for the influence of the catalyst concentration on the selectivity of modified catalysts has not been found. With $HCo(CO)_3PBu_3$, results reported by Rupilius [28] and Tucci [29] are ambiguous. Both authors agree on increasing conversion of olefin and formation of alcohols with increasing catalyst concentration. However, Tucci found no influence on the n/i ratio whereas Rupilius saw improved generation of linear products with increasing catalyst concentration from 1-20g catalyst per mol olefin.

Wilkinson confirmed Rupilius' observations when he showed that for hydroformylation of 1-hexene with $HRh(CO)(PPh_3)_3$ the n/i ratio increased in the catalyst concentration range from 5-50 mmol.(mol^{-1} Rh) [30]. The lower selectivity observed at lower catalyst concentrations is attributed to a further dissociation of $HRh(CO)_2(PPh_3)_2$ to $HRh(CO)_2(PPh_3)$. The loss of phosphine leads to increased formation of the branched product.

In the hydroesterification of cyclohexene, the rate was found to be first order with respect to catalyst concentration (up to 3 $mol.m^{-3}$ palladium concentration).

1.5.4 Ligand concentration

The phosphine-modified catalytic method may be regarded as conservative, as it does not rely on an unknown reactivity of a palladium catalyst in a given catalytic cycle, but rather on ligands which can sustain the catalytically active species even outside of the catalytic cycle [15]. The phosphine-assisted method is the classical and well-established method which gives excellent results in a majority of organometallic processes.

In general, the n/i ratio of modified oxo catalysts increases with increasing ligand/metal ratio [31]. Coordination of ligands to the metal centre enhances the steric bulkiness and hence linear product formation. Depending on the

ligand structure, this effect is more or less pronounced. Kinetically, the catalytic activity varies in a non-linear manner as a function of phosphine concentration [32]. The selectivity of the reaction remains constant above an L/Rh ratio of 10:1 at a point where the activity reaches a maximum.

Tucci reported a linear correlation of the pK_a of monodentate phosphines and the rate of the reaction [29]. The more basic the phosphines, the higher the pK_a hence the less active they are. Due to their strong interaction with the metal, they literally 'block' the metal centre hence lower rates are obtained. With the less basic triphenylphosphine (pK_a = 2.73) rates were almost two orders of magnitude higher than the trialkylphosphine (pK_a = 8.69).

In hydroesterification reactions using $Pd/PPh_3/TsOH$ as catalyst system, the ratio of PPh_3 to Pd has been found to have a significant role in catalyst activity and product selectivity [41]. With styrene, catalytic activity increased up to a PPh_3/Pd ratio of 4 and decreased steadily on further increase. With increasing PPh_3 concentration, PPh_3 competes with the reactant molecules for coordination causing a decrease in activity. A gradual increase in the n/i ratio was observed with an increase in the PPh_3/Pd ratio. It is likely that the palladium centre can have more than one PPh_3, which can increase the steric and electron density at the centre thus resulting in increased formation of the linear product.

1.5.5 Ligand size

At constant ligand/metal ratios, closely related phosphines show lower n/i ratios when their bulkiness is increased [29]. For an example, $P(i\text{-}C_3H_7)_3$ showed 85% linear product in the cobalt-catalysed hydroformylation of 1-hexene whereas with $P(n\text{-}C_3H_7)_3$ 89.5% was achieved. This surprising trend is due to the formation of unsaturated $HM(CO)_2L$ (M = metal; L = ligand) in cases where the bulky group on the ligand is positioned close to the metal. The steric demand of the ligand around the metal favours formation of dicarbonyl species which generate the branched products [14]. This

correlation is only reliable if the ligands being compared have similar electronic structures.

Although triphenylphosphine is much bulkier than $P(n\text{-}C_4H_9)_3$, n/i selectivities of 62.4% and 89.6% respectively, have been reported [29]. It is accepted as a rule of thumb that more basic ligands give higher n/i selectivities "[33]. However, no general rule has been found and so far "no detailed understanding of how phosphines or phosphite control the regiochemistry has emerged".

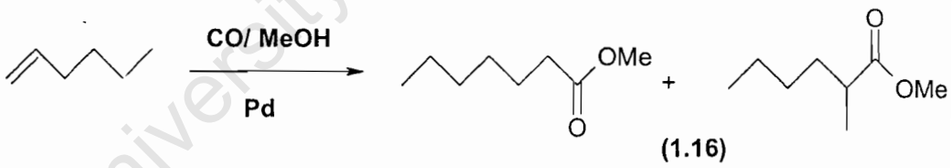
1.6 Hypothesis

Effects of reaction variables on the hydroesterification are similar to those reported for the hydroformylation. The rate of reaction depends directly on the olefin, methanol and palladium concentrations. Regioselectivity of the hydroesterification is influenced by the pressure of carbon monoxide, ligand concentration and size.

1.7. Research proposal

A study on the effects of certain reaction variables on the hydroesterification of 1-hexene over palladium catalyst systems, working at conditions as mild as possible.

Reaction:



(1.16)

Reaction variables include the following:

Temperature

Carbon monoxide pressure

Catalyst concentration

Ligand concentration

Ligand size

Sulfonic acid concentration

as a function of activity and regioselectivity.

2. EXPERIMENTAL

2.1 Materials

Methanol (99.7%) and 1-hexene (99%) purchased from Aldrich were used as received without further purification. $Pd(OAc)_2$ and methanesulfonic acid were used as supplied by Aldrich. Triphenylphosphine (PPh_3) from Aldrich was recrystallised from warm ethanol solution. Carbon monoxide (99.97%) was purchased from Afrox and used without purification.

2.2 Typical procedure for the hydroesterification

The hydroesterification was carried out in a 100 ml Hastelloy autoclave having facilities for gas inlets, outlet, temperature-controlled heating and variable agitation speed. The flow sheet of the experimental set-up is given in Figure 2.1. In a typical experiment, the autoclave was loaded with 0.56 mmol $Pd(OAc)_2$, 3.34 mmol PPh_3, 50 mmol 1-hexene, 0.99 mol methanol and 25.6 mmol methanesulfonic acid making the total reaction volume 42 ml. The autoclave was pressure tested with 90 bar nitrogen and then slowly depressurised. The contents of the autoclave were heated to reaction temperature (90°C) with stirring. At reaction temperature, carbon monoxide (65 bar) was introduced into the autoclave through the by-pass line. The autoclave was subsequently pressurised with carbon monoxide to 70 bar through the ballast vessel with stirring (1200 rpm). The reaction was carried out at a constant pressure by feeding carbon monoxide from the ballast vessel. The progress of the reaction was monitored by measuring the decrease in pressure of carbon monoxide in the ballast vessel (1 litre) as a function of time which is linked to a personal computer equipped with software recording the pressure drop and temperature variations in the ballast vessel per second.

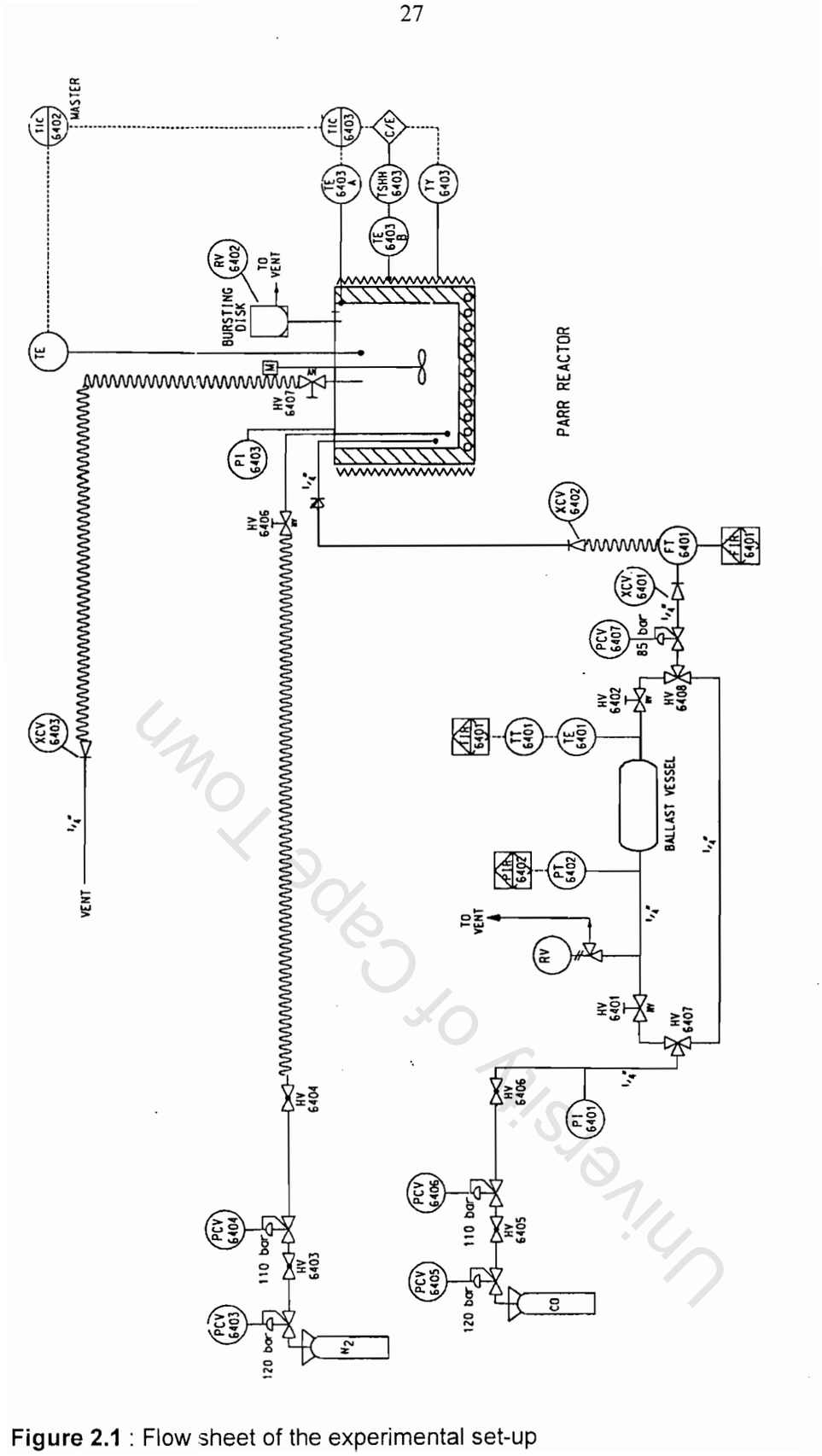


Figure 2.1 : Flow sheet of the experimental set-up

At the end of the reaction period (1 h), the autoclave was allowed to cool to room temperature and was slowly depressurised. The liquid phase was quantitatively analysed for reactants and products by Gas Chromatography. Compositions of reaction products were confirmed by GC-MS.

2.3 Analysis

Analyses of organic product samples was performed on a Hewlett-Parkard 5890 Series II model gas chromatographic unit linked to a personal computer equipped with Class-VP software for recording and integration of the chromatograms. A 50-meter PONA (Cross-linked Methyl Siloxane) column of 0.2 millimetre internal diameter and 0.50 microns film thickness was utilised for separation. A flame ionisation detector (FID) was used for detection of reaction components utilising nitrogen as the carrier gas. The operating conditions of the GC are outlined in Table 2.1.

Table 2.1 : Operating conditions of the GC

Operational parameter	**Condition**
Carrier gas (CG)	Nitrogen
Detector	FID
Initial temperature	50 °C
Initial isothermal period	5 min
Rate	10 °C/min
Final temperature	180 °C
Final isothermal period	5 min
Column head pressure	1.7 bar
Split ratio	90:1
Injector temperature	230 °C
Detector temperature	250 °C

2.4 Data evaluation

In the determination of the turnover frequency, it is assumed that 1 mole of CO consumed produces 1 mole of an ester product compound. The turnover frequency is then determined from the amount of CO, which was delivered from the ballast vessel during the initial fifteen minutes. The number of moles of CO consumed during this period was determined by the pressure-drop in the ballast vessel. Using the ideal gas law, the turn-over-frequency (moles of product formed per mole palladium per hour) is calculated:

$$TOF = \frac{n_{CO,consumed}}{n_{Pd} \bullet 0.25hr} \qquad \frac{\text{mol}}{\text{mol} \cdot \text{hr}}$$

with

$n_{CO,consumed}$: number of moles of CO consumed in the first 15 minutes as calculated from the pressure drop in the ballast vessel using the ideal gas law

n_{Pd} : number of moles Pd loaded in the reactor

$$TOF = \frac{n_{CO,consumed,initial}}{n_{Pd} \bullet 0.25hr} = \frac{V_{ballast}}{n_{Pd}} \bullet \frac{1}{RT} \bullet \left(\frac{\Delta P}{\Delta t}\right)_{initial}$$

Initial time = Initial 15 minutes

The conversion of peak areas into amounts of the corresponding sample components was effected via response factors, which are related to the unit weight of the detected compound. In determining the response factors, an internal standard (toluene, 1g, with a weight response factor of 1.07) was added to a sample of single composition at an accurately known concentration determined by weighing.

Table 2.2 : Response factors by weight for gas chromatographic evaluation of data using FID

Compound	Response factor
1-hexene	0.796 ± 0.025
Methyl acetate	0.2635 ± 0.012
cis & trans 2-hexene	0.8352 ± 0.023
3-hexene	0.8582 ±0.031
Methylheptanoate	0.5531 ± 0.008
Methanol	0.2420 ± 0.005

The determination of the number of moles of a certain compound in the reaction mixture was achieved by GC-analysis of the product composition. The mixture was then analysed. The number of moles of a certain compound was determined from the peak areas. The quantitative analysis of the reaction mixture based on the response factor correction was accomplished through the formula [50].

$$n_i = \frac{A_i \cdot G_{st} \cdot R_{f,i}}{A_{st} \cdot R_{f,st}} \bullet \frac{1}{M_i}$$

where

n_i = moles of compound i

A_i = Peak area of compound i

G_{st} = Mass of internal standard

$R_{f,i}$ = Response factor of compound i

A_{st} = Peak area of internal standard

$Rf_{,st}$ = Response factor of internal standard

M_i = Molar mass of compound i

It was assumed that all C8-esters have identical response factors (0.5531 ± 0.008).

The conversion of 1-hexene was calculated as follows:

$$X = 1 - \frac{n_{1-hexene,out}}{n_{1-hexene,added}} .100\%$$

The selectivity to a certain compound was expressed as follows:

$$S_P = \frac{n_{P,formed}}{n_{1-hexene,consumed}} \cdot 100\% \text{ in mol-\%}$$

Various esters are formed in the hydro-esterification of 1-hexene, i.e. methylheptanoate, methyl-2-methylhexanoate and methyl-2-ethylpentanoate. In order to evaluate the relative amounts of the various esters as a function of the reaction conditions, the content of an ester in the fraction of esters is defined (units in mol-%):

$$C_{n-ester} = \frac{n_{methylhep\,tan\,oate}}{n_{totalesters}} \cdot 100\%$$

$$C_{i-ester} = \frac{n_{methyl-2-methyl-hexanoate}}{n_{totalesters}} \cdot 100\%$$

$$C_{i'-ester} = \frac{n_{methyl-2-ethyl-pen\,tan\,oate}}{n_{totalesters}} \cdot 100\%$$

where $n_{totalesters} = n_{methylheptanoate} + n_{methyl-2-methyl-hexanoate} + n_{methyl-2-ethyl-pentanoate}$

Furthermore, the molar ratio of methylheptanoate to methyl-2-methyl-hexanoate (n:i ratio) is evaluated.

The presence of 2-hexene and 3-hexene was evidence to isomerisation of 1-hexene to internal olefins. To evaluate the relative amounts of internal olefins, selectivities to 2-hexene and 3-hexene were calculated. The rate of double-bond isomerisation was expressed as follows:

$$r_{DB} = \frac{S_I}{S_E} \bullet TOF \quad \frac{mol}{mol \bullet hr}$$

where

S_I = Selectivity to internal olefin I

S_E = Selectivity to C-8 esters

TOF = Activity as determined from the number of CO molecules consumed

3. RESULTS

3.1 Catalyst system

The catalyst system used in the hydroesterification of 1-hexene is a mixture of $Pd(OAc)_2/PPh_3$/methanesulfonic acid, in the molar ratio of 1/6/46 unless otherwise stated, from which the active catalyst species was formed *in situ*. A yellow complex is generated on reaction of $Pd(OAc)_2$ with PPh_3 in 1-hexene. On subsequent reaction with methanesulfonic acid, the colour of the solution changes to brown

3.2 Investigation using standard conditions

The performance of the *in-situ* generated, catalytic system is evaluated in terms of activity (turnover frequency, TOF) and the selectivity towards the various product compounds.

3.2.1 Establishment of a base-case reaction

In order to establish a base case, from which the effect of the reaction conditions on the activity and selectivity can be judged, the hydroesterification was performed at the conditions given in Table 3.1.

The base case run was repeated three times to determine the reproducibility of these runs. Figure 3.1 shows the activity of the catalyst as a function of reaction time. The number of moles of CO consumed as determined from the pressure drop in the ballast vessel relative to the number of moles of 1-hexene initially present in the system was taken as a measure of the catalytic activity. The tangent to the observed curve represents the rate of CO consumption, and thus the rate of 1-hexene consumption for the formation of esters, as a function of reaction time.

Table 3.1 : Base conditions for the hydroesterification of 1-hexene with $Pd(OAc)_2/PPh_3$/methanesulfonic acid, from which the active catalyst species was formed *in situ*, at 90°C (stirring speed: 1000 rpm)

			$n_i/n_{1\text{-hexene}}$	**Comments**
Feed	1-hexene	50 mmol	1.0	
	Methanol	0.99 mol	19.8	Large excess
	CO	70 bar		Kept constant
Catalyst	$Pd(OAc)_2$	0.56 mmol	0.011	
	PPh_3	3.36 mmol	0.066	PPh_3:Pd=6
	Methanesulfonic acid (MsOH)	25.6 mmol	0.52	MsOH:Pd = 46

The number of moles of CO- converted relative to the initial number of moles of 1-hexene present in the system increases initially linearly with time. After a reaction time of ca. 15 minutes the rate of consumption of CO, and thus the rate of consumption of 1-hexene drops significantly. The drop in the rate of reaction is more significant than would have been expected, if the rate of reaction is first order with respect to 1-hexene.

Internal olefins were detected in the reaction mixture. The formation of methyl-2-ethylpentanoate was observed. This suggests initial isomerisation of 1-hexene to internal hexene followed by hydroesterification yielding the ester. This is also reflected in the low selectivity for the formation of esters (average selectivity to the ester products of 44 mol-%). The observed normal-to branched ratio was 1.1:1.

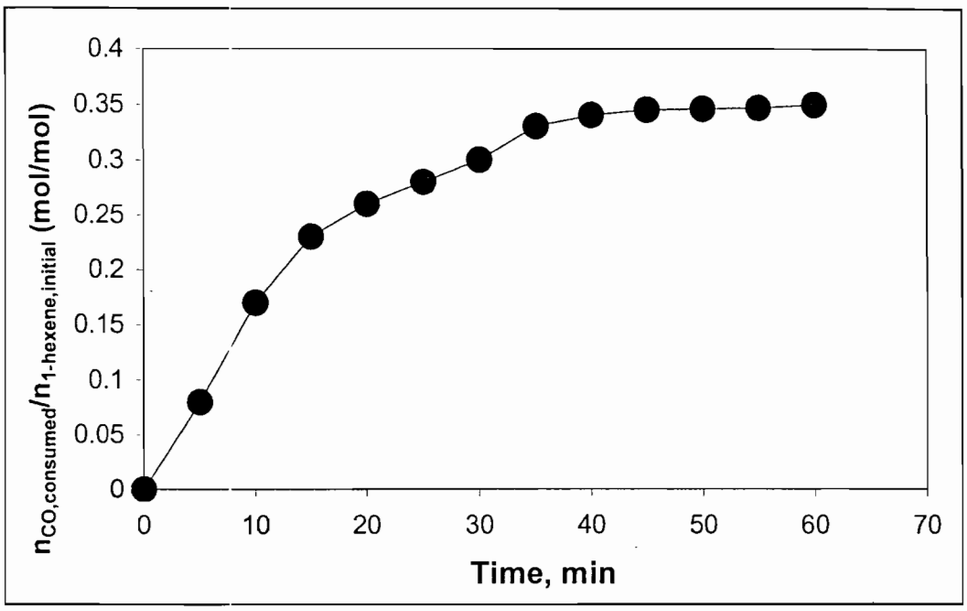


Figure 3.1 : The catalytic activity, measured as the number of moles of CO consumed relative to the number of moles of 1-hexene initially in the system as a function of reaction time for the base case runs ($T_{reaction}$ = 90°C; p_{CO} = 70 bar; $n_{1\text{-hexene}}$=50 mmol; $n_{methanol}$=0.99 mol; n_{Pd}=0.56 mmol; Pd: PPh_3 : methanesulfonic acid = 1:6:46)

The turnover frequency, as determined from the number of moles of CO consumed during the first 15 minutes of the reaction, and the selectivity for the base case run at the end of the reaction (reaction time of 60 minutes) are given in Table 3.2. The compounds identified during the base case run are given in Appendix A1.

Table 3.2 : Activity (turnover frequency, TOF, determined from the number of moles of CO converted during the initial 15 minutes) and selectivity in the 1-hexene hydroesterification after a reaction time of 60 minutes under the base case conditions ($T_{reaction}$ = 90°C; p_{CO} = 70 bar; $n_{1\text{-hexene}}$=50 mmol; $n_{methanol}$=0.99 mol; n_{Pd}=0.56 mmol; Pd: PPh_3 : methanesulfonic acid = 1:6:46; stirring speed: 1000 rpm)

Run	TOF hr^{-1}	$S_{2\text{-hexene}}$ mol-%	$S_{3\text{-hexene}}$ mol-%	S_{ester} mol-%	$C_{n\text{-ester}}$ mol-%	$C_{i\text{-ester}}$ mol-%	$C_{i'\text{-ester}}$ mol-%	n:i
1	105	48	12	40	52	40	8	1.3:1
2	101	38	10	52	43	47	10	0.9:1
3	101	50	10	40	49	44	7	1.1:1
Average	**102±3**	**45±7**	**11±1**	**44±8**	**48±5**	**44±4**	**8±1**	**1.1:1**

The reproducibility of the run is acceptable. The average turnover frequency for the hydroesterification of 1-hexene using the catalyst precursor in the ratio Pd/ PPh_3/ MsOH of 1/6/46 at 90°C and 70 bar carbon monoxide pressure, was 102±2 moles of product esters per mole of palladium per hour. The 1-hexene conversion after a reaction time of 60 minutes was 35 % which is expected based on a constant TOF in the first 15 minutes followed by a strong decline in the turnover frequency (see Fig. 3.1).

3.2.2 Mass transport limitations

In order to ensure that the measurements are not falsified by gas-to-liquid mass transport limitations, the stirring speed in the base case reaction was varied between 800 and 1400 rpm (see Table 3.3). At lower stirring speed the gas-liquid mass transfer might limit the rate of reaction. At a very high stirring speed the formation of a large vortex may also induce mass transport limitations since gas introduction was at the bottom of the autoclave.

Table 3.3: Effect of stirring speed on activity (turnover frequency, TOF, determined from the number of moles of CO converted during the initial 15 minutes) and selectivity in the 1-hexene hydroesterification after a reaction time of 60 minutes ($T_{reaction}$ = 90°C; p_{CO} = 70 bar; $n_{1\text{-hexene}}$=50 mmol; $n_{methanol}$=0.99 mol; n_{Pd}=0.56 mmol; Pd: PPh_3 : methanesulfonic acid = 1:6:46)

Stirring speed rpm	TOF hr^{-1}	$S_{2\text{-hexene}}$ mol-%	$S_{3\text{-hexene}}$ mol-%	S_{ester} mol-%	$C_{n\text{-ester}}$ mol-%	$C_{i\text{-ester}}$ mol-%	$C_{i'\text{-ester}}$ mol-%	n:i
800	101	50	10	40	48	43	9	1.1:1
1000	102	45	11	44	48	43	9	1.1:1
1200	106	52	13	35	54	39	7	1.4:1
1400	128	43	9	48	47	43	10	1.1:1

A stirring speed between 800 and 1200 rpm does not seem to affect the rate of the reaction significantly. An increase in the turnover frequency is observed with a higher stirring speed of 1400 rpm. This might be due to the formation of a vortex which causes mass-transfer limitations thus a low concentration of carbon monoxide in the liquid phase. This would result in an increase in the reaction rate (TOF) if the reaction is inhibited by carbon monoxide.

3.3 Effects of reaction parameters

3.3.1 Effect of 1-hexene concentration

The effect of the 1-hexene concentration was investigated at 90°C and p_{CO} = 70 bar by changing the initial number of moles of 1-hexene charged to the autoclave (see Table 3.4). This leads to a simultaneous increase in the reaction volume. In the base case, the initial concentration of 1-hexene was 1.25 mol/litre. An increase in the 1-hexene concentration from 1.25 to 3.13 mol/litre at 90°C leads to an increase in the turnover frequency from 102 to 250 hr^{-1}.

Table 3.4 : Effect of the initial concentration of 1-hexene on the turnover frequency (TOF, determined from the number of moles of CO converted during the initial 15 minutes) and selectivity in the 1-hexene hydroesterification after a reaction time of 60 minutes ($T_{reaction}$ = 90°C; p_{CO} = 70 bar; $n_{methanol}$=0.99 mol; n_{Pd}=0.56 mmol; Pd: PPh_3 : methanesulfonic acid = 1:6:46; stirring speed: 1000 rpm)

[1-hexene] mol/litre	TOF hr^{-1}	r_{DB} hr^{-1}	$S_{2\text{-hexene}}$ mol-%	$S_{3\text{-hexene}}$ mol-%	S_{ester} mol-%	$C_{n\text{-ester}}$ mol-%	$C_{i\text{-ester}}$ mol-%	$C_{i'\text{-ester}}$ mol-%	n:i
1.25	102	130	45	11	44	48	44	8	1.1:1
1.88	188	101	28	7	65	46	45	9	1:1
2.50	243	90	15	12	73	63	32	5	2:1
3.13	250	71	18	4	78	64	31	5	2.1:1

The reaction rate of CO consumption can be reasonably approximated to be first-order (see Figure 3.2), with a first order rate constant of 89 litre/ (mol Pd·hr).

$-r_{CO} = k' \cdot [1-\text{hexene}]$ with k'= 89 litre/(mol Pd·hr)

(correlation coefficient R^2:0.876)

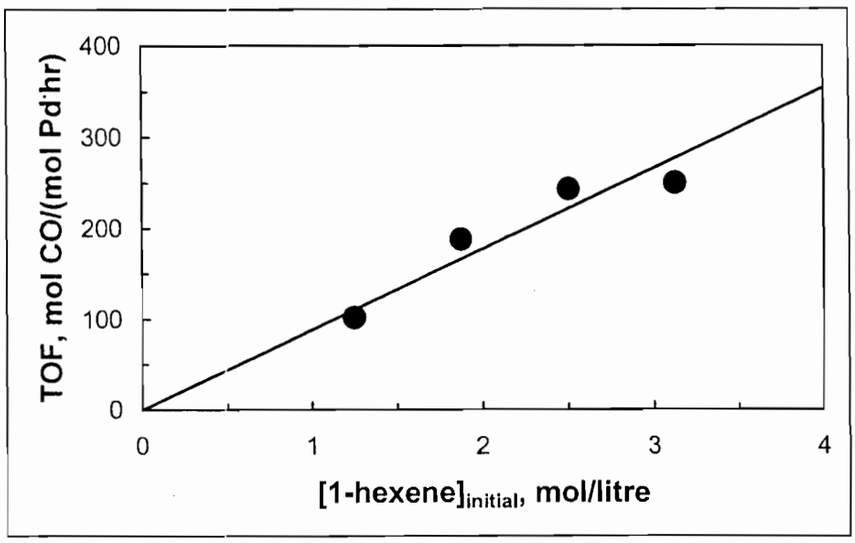


Figure 3.2 : The turnover frequency (TOF) as a function of the initial concentration of 1-hexene ($T_{reaction}$ = 90°C; p_{CO} = 70 bar; $n_{methanol}$=0.99 mol; n_{Pd}=0.56 mmol; Pd: PPh_3 : methanesulfonic acid = 1:6:46; stirring speed: 1000 rpm). Solid line represents best fit to first order reaction

The deviation observed at high 1-hexene concentration might be attributed to an inhibition of the rate of hydroesterification by 1-hexene, but presently there are not sufficient data to justify the incorporation of an inhibition term in the rate expression.

Enhanced ester formation was observed at higher 1-hexene concentrations. Similarly, selectivity to normal and branched esters was high at high 1-hexene concentrations. Higher n-to-i ratios were also obtained at high 1-hexene concentrations. Increasing the 1-hexene concentration resulted in a decrease in the rate of double-bond isomerisation. Thus the selectivity for double-bond isomerisation decreases as well.

3.3.2 Effect of carbon monoxide pressure

The effect of the carbon monoxide partial pressure was investigated at a constant temperature of 90°C using the catalyst system in the ratio $Pd/PPh_3/MsOH$ = 1:6:46 (see Table 3.5).

Table 3.5: Effect of the carbon monoxide partial pressure on the turnover frequency (TOF, determined from the number of moles of CO converted during the initial 15 minutes) and selectivity in the 1-hexene hydroesterification after a reaction time of 60 minutes ($T_{reaction}$ = 90°C; $n_{1\text{-hexene}}$=50 mmol; $n_{methanol}$=0.99 mol; n_{Pd}=0.56 mmol; Pd: PPh_3 : methanesulfonic acid = 1:6:46; stirring speed: 1000 rpm)

p_{CO} bar	TOF hr^{-1}	$S_{2\text{-hexene}}$ mol-%	$S_{3\text{-hexene}}$ mol-%	S_{ester} mol-%	$C_{n\text{-ester}}$ mol-%	$C_{i\text{-ester}}$ mol-%	$C_{i'\text{-ester}}$ mol-%	n:i
10	276	24	6	70	73	23	4	3.2:1
20	233	27	6	67	71	25	4	2.8:1
30	191	45	7	48	60	32	6	1.9:1
50	111	38	7	55	60	35	5	1.7:1
70	102	45	11	44	48	43	9	1.1:1
90	105	14	33	53	45	47	8	1:1

In the base case (see Table 3.1) the carbon monoxide partial pressure was 70 bar. A decrease in the CO partial pressure at 90°C to 10 bar leads to a significant increase in the turnover frequency. Thus, CO strongly inhibits the hydroesterification of 1-hexene. The dependency of the rate of reaction on the carbon monoxide partial pressure can be modelled as:

$$-r_{CO} = \frac{k'' \cdot p_{CO}}{(a + K \cdot p_{CO})^2} \qquad \text{with} \quad \frac{k}{a^2} = 158 \text{ mol CO/ (bar·hr·mol Pd)}$$

$$\frac{k}{K^2} = 8.2\ 10^3 \text{ (mol CO·bar)/(hr·mol Pd)}$$

(correlation coefficient R^2: 0.991; see Figure 3.3)

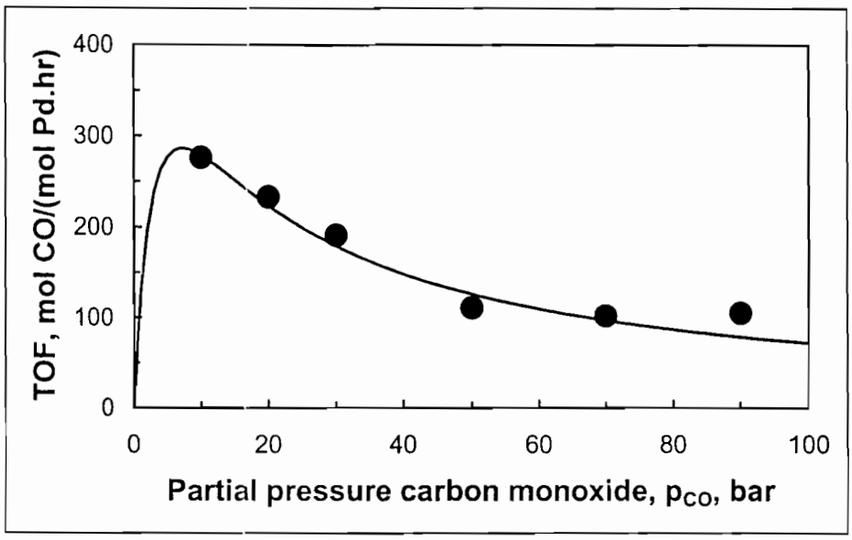


Figure 3.3 : The turnover frequency (TOF) as a function of the partial pressure of carbon monoxide ($T_{reaction}$ = 90°C; $n_{methanol}$=0.99 mol; $n_{1\text{-hexene}}$=50 mmol; n_{Pd}=0.56 mmol; Pd: PPh_3 : methanesulfonic acid = 1:6:46; stirring speed: 1000 rpm). Solid line represents best fit to the rate expression $-r_{CO} = \frac{k'' \cdot p_{CO}}{(a + K \cdot p_{CO})^2}$

The selectivity for the formation of esters decreases with increasing carbon monoxide partial pressure. Thus, the selectivity for double-bond isomers, 2-hexene and 3-hexene, is high at high carbon monoxide partial pressure. This indicates that the double-bond isomerisation is not affected as strongly as the hydroesterification by the partial pressure of carbon monoxide. It might thus be concluded that the double-bond isomerisation does not proceed at the same catalytic centre responsible for the hydroesterification. The double-bond isomerisation might be acid catalysed, i.e. homogeneously catalysed by the presence of methanesulfonic acid or by a different Pd-complex.

The larger concentration of double bond isomers with increasing carbon monoxide partial pressure leads to a decrease in the methylheptanoate content in the fraction of esters, due to the larger concentration of 2- and 3-hexene in the reaction mixture. The hydroesterification of the 2- and 3-hexene

will lead to the formation of methyl-2-methylhexanoate and methyl-ethylpentanoate.

3.3.3 Effect of methanol concentration

The effect of methanol concentration was studied by adding the non-coordinating and low polar solvent, toluene, to the required liquid phase volume of 48ml (see Table 3.6).

Table 3.6 : Effect of initial methanol concentration on the turnover frequency (TOF, determined from the number of moles of CO converted during the initial 15 minutes) and selectivity in the 1-hexene hydroesterification after a reaction time of 60 minutes ($T_{reaction}$=90°C; p_{CO} = 70 bar; $n_{1\text{-hexene}}$=50 mmol; $V_{liquid\ phase}$ = 48 ml; make-up solvent: toluene; n_{Pd}=0.56 mmol; Pd: PPh_3 : methanesulfonic acid = 1:6:46; stirring speed: 1000 rpm)

[methanol] mol/litre	TOF hr^{-1}	$S_{2\text{-hexene}}$ mol-%	$S_{3\text{-hexene}}$ mol-%	S_{ester} mol-%	$C_{n\text{-ester}}$ mol-%	$C_{i\text{-ester}}$ mol-%	$C_{i'\text{-ester}}$ mol-%	n:i
2.5	132	56	15	29	48	41	11	1.2:1
5.2	148	45	5	50	46	46	8	1:1
7.7	340	34	6	60	64	31	5	2.0:1
10.3	269	29	5	66	61	33	6	2.1:1
15.5	222	46	7	47	56	36	8	1.6:1
23.6	102	45	11	44	48	43	9	1.1:1

The turnover frequency passes a pronounced maximum at an initial methanol concentration of 7.7 mol/litre (see Figure 3.4). This sharp maximum cannot be satisfactorily modelled with a single kinetic expression. At low methanol concentration the turnover frequency seems to be directly proportional to the methanol concentration. At high methanol concentration the reaction becomes inhibited by methanol. Traces of palladium-black were observed at high methanol concentrations.

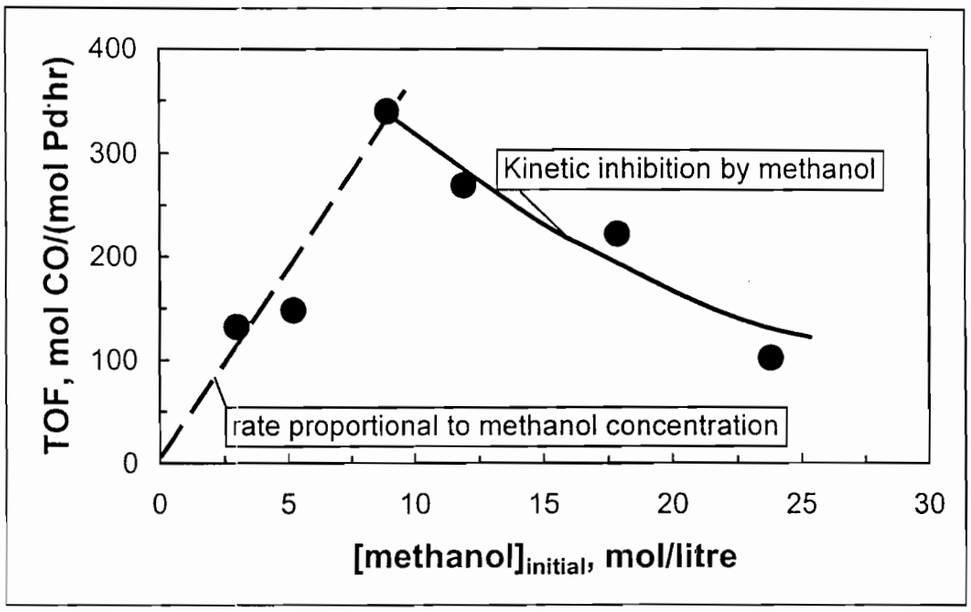


Figure 3.4 : The turnover frequency (TOF) as a function of the initial methanol concentration ($T_{reaction}$ = 90°C; p_{CO}=70 bar; $n_{1\text{-hexene}}$=50 mmol; $V_{liquid\ phase}$ = 48 ml; make-up solvent: toluene; n_{Pd}=0.56 mmol; Pd: PPh_3 : methanesulfonic acid = 1:6:46; stirring speed: 1000 rpm).

A similar trend was observed for the selectivity for the formation of esters, which is maximum at an initial concentration of methanol of ca. 10 mol/litre. The n-to-i ratio was higher in the range of a molar ratio 7.7-15.

3.3.4 Effect of reaction temperature

The effect of temperature on catalyst activity and selectivity was studied at a constant carbon monoxide pressure of 70 bar using the catalyst system in the ratio Pd/PPh_3/MsOH = 1:6:46 (see Table 3.7). The reaction at 70°C could not be reproduced. Above 110 °C, the catalyst partially decomposed to palladium black. At 150 °C, the catalyst totally decomposed to inactive palladium black.

Table 3.7 : Effect of reaction temperature on the turnover frequency (TOF, determined from the number of moles of CO converted during the initial 15 minutes) and selectivity in the 1-hexene hydroesterification after a reaction time of 60 minutes (p_{CO} = 70 bar; $n_{1\text{-hexene}}$= 50 mmol; $n_{methanol}$=0.99 mol; n_{Pd}=0.56 mmol; Pd: PPh_3 : methanesulfonic acid = 1:6:46; stirring speed: 1000 rpm)

$T_{reaction}$ °C	TOF hr^{-1}	$S_{2\text{-hexene}}$ mol-%	$S_{3\text{-hexene}}$ mol-%	S_{ester} mol-%	$C_{n\text{-ester}}$ mol-%	$C_{i\text{-ester}}$ mol-%	$C_{i'\text{-ester}}$ mol-%	n:i
50	28	39	46	15	68	27	5	2.5:1
50	34	50	37	13	70	23	7	3.0:1
90	102	45	11	44	48	43	9	1.1:1
110	106	30	7	63	57	37	6	1.5;1
130	105	35	5	60	70	25	5	2.8:1
150	0	-	-	-	-	-	-	-

The (partial) transformation of the catalytically active complex to palladium black makes it difficult to estimate the true temperature dependency of the turnover frequency of the hydroesterification of 1-hexene. In the temperature range between 50 and 90°C an observed activation energy of 30 kJ/mol was determined.

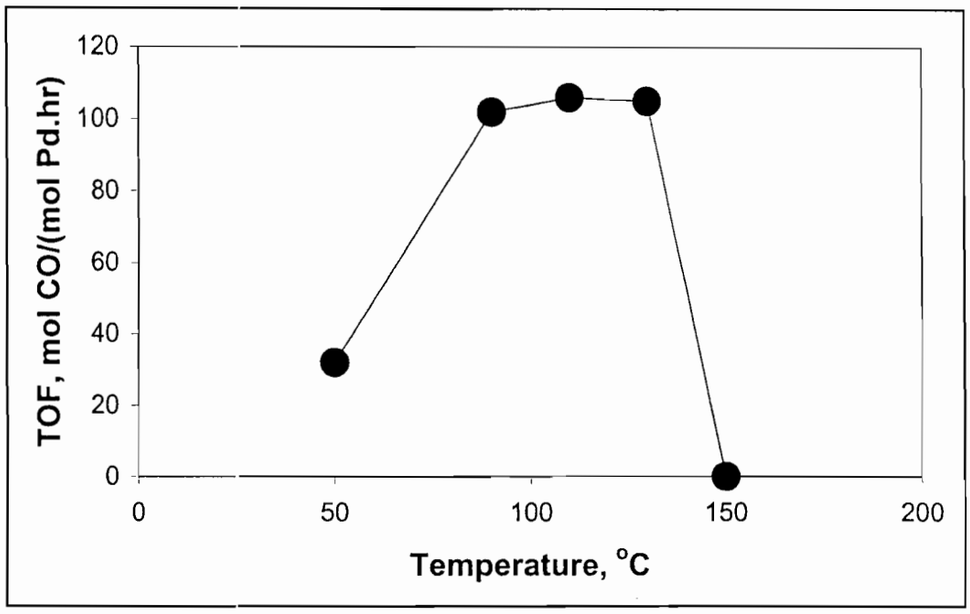


Figure 3.5 : The turnover frequency (TOF) as a function of temperature (p_{CO} = 70 bar ; $n_{methanol}$=0.99 mol; $n_{1\text{-}hexene}$=50 mmol; n_{Pd}=0.56 mmol; Pd: PPh_3 : methanesulfonic acid = 1:6:46; stirring speed: 1000 rpm).

3.4 Effect of catalyst parameters

3.4.1 Effect of palladium concentration

The amount of catalyst added to the system was varied at a reaction temperature of 90°C and 70 bar carbon monoxide pressure keeping the molar ratio of $Pd/PPh_3/MsOH$ constant at 1:6:46 (see Table 3.8). The turnover frequency, which is expressed per mol of Pd, is expected to be independent of the amount of palladium added to the system, if a constant fraction of the available palladium is being used to form the catalytically active complex. A high turnover frequency observed at low palladium concentration, which decreases with increasing palladium concentration suggesting that a lower fraction of palladium is actually used for the formation of the catalytically active complex with increasing palladium concentration. This might be attributed to the formation of larger palladium clusters (and even palladium black), which is favoured at high palladium concentrations.

Table 3.8 : Effect of amount of palladium on the turnover frequency (TOF, determined from the number of moles of CO converted during the initial 15 minutes) and selectivity in the 1-hexene hydroesterification after a reaction time of 60 minutes ($T_{reaction}$=90°C; p_{CO} = 70 bar; $n_{1\text{-hexene}}$=50 mmol; $n_{methanol}$=0.99 mol; Pd: PPh_3 : methanesulfonic acid = 1:6:46; stirring speed: 1000 rpm)

n_{Pd} mmol	TOF hr^{-1}	r_{DB}	$S_{2\text{-hexene}}$ mol-%	$S_{3\text{-hexene}}$ mol-%	S_{ester} mol-%	$C_{n\text{-ester}}$ mol-%	$C_{i\text{-ester}}$ mol-%	$C_{i'\text{-ester}}$ mol-%	n:i
0.005	0	-	-	-	-	-	-	-	-
0.05	265	1502	80	5	15	56	38	6	1.5:1
0.56	102	130	45	11	44	48	44	8	1.1:1
0.81	104	82	37	7	56	54	39	7	1.4:1
1.07	87	58	32	8	60	43	47	10	0.9:1

The selectivity for ester formation increases with increasing palladium concentration. Lower rates of isomerisation were observed with increasing palladium concentration. Though lower activities were obtained at high palladium concentrations, the selectivity to ester formation was enhanced.

3.4.2 Effect of ligand

3.4.2.1 Effect of ligand concentration

Triphenylphosphine was the ligand of choice for the catalyst for the hydroesterification of 1-hexene. The molar ratio of triphenylphosphine to palladium was varied at 90°C and 70 bar carbon monoxide pressure at the ratio Pd:MsOH = 1:46 (see Table 3.9).

Table 3.9 : Effect of molar ratio of triphenylphosphine to palladium on the turnover frequency (TOF, determined from the number of moles of CO converted during the initial 15 minutes) and selectivity in the 1-hexene hydroesterification after a reaction time of 60 minutes ($T_{reaction}$=90°C; p_{CO} = 70 bar; $n_{1\text{-hexene}}$=50 mmol; $n_{methanol}$=0.99 mol; n_{Pd}=0.56 mmol; Pd: methanesulfonic acid = 1:46; stirring speed: 1000 rpm)

n_{PPh3}/n_{Pd} mol/mol	TOF hr^{-1}	$S_{2\text{-hexene}}$ mol-%	$S_{3\text{-hexene}}$ mol-%	S_{ester} mol-%	$C_{n\text{-ester}}$ mol-%	$C_{i\text{-ester}}$ mol-%	$C_{i'\text{-ester}}$ mol-%	n:i
2	57	74	20	6	36	55	9	0.7:1
6	102	45	11	44	48	44	8	1.1:1
8	212	0[1]	0[1]	100	72	24	4	3:1
10	229	4	6	90	70	25	5	2.8:1
20	391	6	6	88	74	23	3	3.2:1
30	408	10	7	83	75	21	4	3.6:1
46	211	32	20	48	75	21	4	3.6:1

1. Below detection limits

The molar ratio of triphenylphosphine to palladium has a significant role in the catalyst activity and product selectivity. No catalytic activity was observed without the triphenylphosphine ligand and complete precipitation of palladium metal results under such experimental conditions (see Figure 3.6). Even at a molar ratio of triphenylphosphine to palladium of 2, substantial precipitation of the active catalyst to palladium metal was noticed. No significant metal deposition was observed at ratios higher than eight. The turnover frequency increases up to a molar ratio of triphenylphosphine to palladium of approximately 30 indicating the need for a large excess of the ligand for the formation of the catalytically, active complex. At higher triphenylphosphine to palladium ratios the turnover frequency decreases. This might be attributed to the inhibition of the formation of the intermediate complex and/or competition with the reagents for coordination to the metal centre.

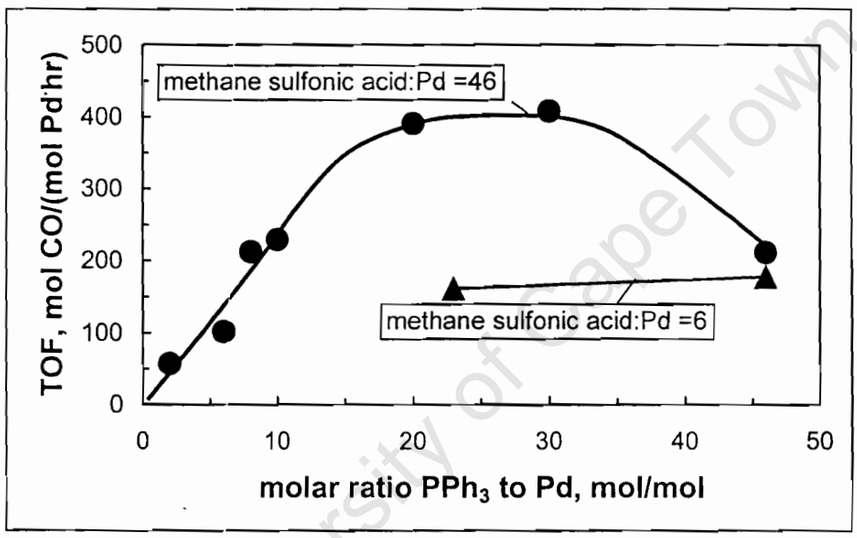


Figure 3.6 : The turnover frequency (TOF) as a function of the molar ratio of triphenylphosphine to palladium ($T_{reaction}$ = 90°C; p_{CO}=70 bar; $n_{1\text{-}hexene}$=50 mmol; $n_{methanol}$=0.99 mol; n_{Pd}=0.56 mmol; stirring speed: 1000 rpm).

The selectivity for the formation of esters also passes a maximum with increasing molar ratio of triphenylphosphine to palladium. The selectivity for the formation of the ester reflects the extent to which the reaction takes place over the palladium complex versus the extent of non-ligand catalysed reaction. Thus, a high selectivity for the formation of esters is obtained, when a maximum amount of the catalytically, active complex is available.

The methylheptanoate content in the fraction of esters increases with increasing molar ratio of triphenylphosphine to palladium and consequently the n:i ratio increases as well. This reflects the relative high concentration of double-bond isomers in the liquid reaction medium at low molar ratios of triphenylphosphine to palladium. At low molar ratios of triphenylphosphine to palladium the concentration of the double-bond isomers is high resulting in low concentrations of the methylheptanoate.

The effect of the molar ratio of triphenylphosphine to palladium was also investigated at a lower level of methanesulfonic acid (molar ratio of methanesulfonic acid to palladium of 6 – see Table 3.10). The activity at this level of methanesulfonic acid is at a molar ratio of triphenylphosphine to palladium of 23 is much reduced, whereas the activity at the high molar ratio of triphenylphosphine to palladium is approximately identical to the activity obtained at the high level of methanesulfonic acid. It is also observed at the low methanesulfonic acid ratio to palladium, that with increasing molar ratio of triphenylphosphine to palladium the selectivity for the formation of the esters increases, whereas the methylheptanoate content in the fraction of the esters remain constant. It should however, be noted that with decreasing the molar ratio of methanesulfonic acid to palladium leads to a much lower selectivity for the formation of the esters.

Table 3.10 : Effect of molar ratio of triphenylphosphine to palladium on the turnover frequency (TOF, determined from the number of moles of CO converted during the initial 15 minutes) and selectivity in the 1-hexene hydroesterification after a reaction time of 60 minutes ($T_{reaction}$=90°C; p_{CO} = 70 bar; $n_{1\text{-hexene}}$=50 mmol; $n_{methanol}$=0.99 mol; n_{Pd}=0.56 mmol; Pd: methanesulfonic acid = 1:6; stirring speed: 1000 rpm)

n_{PPh3}/n_{Pd} mol/mol	TOF hr^{-1}	$S_{2\text{-hexene}}$ mol-%	$S_{3\text{-hexene}}$ mol-%	S_{ester} mol-%	$C_{n\text{-ester}}$ mol-%	$C_{i\text{-ester}}$ mol-%	$C_{i'\text{-ester}}$ mol-%	n:i
23	161	41	0	59	72	23	5	3.1:1
46	177	17	9	74	78	19	3	4.0:1

3.4.2.2 Variation of the type of ligand

The effect of different ligands on catalytic activity was studied at base-case conditions at the molar ratio of palladium to ligand to methanesulfonic acid of 1: 6:46 and 1:30:46 (see Table 3.11). No catalytic activity was observed with tri(o-tolyl)phosphine as a ligand.

Diphenyl-2-pyridylphosphine and tris(p-methoxyphenyl)phosphine, were tested at low concentrations. The latter gave the best activity at the molar ratio of metal:ligand of 1:6. The highest ester formation was attained with triphenylphosphine at a molar ratio of 30. Higher n-to-i ratios were observed with these ligands though lower than those obtained with PPh_3 at molar excess of 30. At a molar excess of 30 the PPh_3 gave the highest degree of hydroesterification.

Table 3.11 : Effect of type of ligand on the turnover frequency (TOF, determined from the number of moles of CO converted during the initial 15 minutes) and selectivity in the 1-hexene hydroesterification after a reaction time of 60 minutes ($T_{reaction}$=90°C; p_{CO} = 70 bar; $n_{1\text{-hexene}}$=50 mmol; $n_{methanol}$=0.99 mol; n_{Pd}=0.56 mmol; Pd: methanesulfonic acid = 1:6; stirring speed: 1000 rpm)

Ligand	n_{ligand}/n_{Pd} mol/mol	TOF hr^{-1}	$S_{2\text{-hexene}}$ mol-%	$S_{3\text{-hexene}}$ mol-%	S_{ester} mol-%	$C_{n\text{-ester}}$ mol-%	$C_{i\text{-ester}}$ mol-%	$C_{i'\text{-ester}}$ mol-%	n:i
PPh_3[1]	6	102	45	11	44	48	44	8	1.1:1
PR_1[2]	6	35	82	9	10	63	32	5	2.0:1
PR_2[3]	6	273	38	7	55	69	27	4	2.5:1
PBu_3[4]	30	26	85	8	7	0	100	0	0:1
PPh_3[2]	30	408	10	7	83	75	21	4	3.6:1
$P(OPh)_3$	30	18	36	40	24	0	100	0	0:1

[1]PPh_3: triphenylphosphine at molar excess 6;

[2]PPh_3: triphenylphosphine at molar excess 30;

[2]PR_1: diphenyl-2-pyridylphosphine;

[3]PR_2: tris(p-methoxyphenyl)phosphine;

[4]PBu_3: tributylphosphine;

$P(OPh)_3$: triphenylphosphite;

Ligand effect studies are hard to interpret, because for a particular ligand the rates may differ by at least an order of magnitude, depending on the concentration of palladium, ligand and carbon monoxide. At a high molar ratio of ligand to palladium, the activity was found to decrease in the order PPh_3 >> PBu_3 > $P(OPh)_3$ > $P(o\text{-tol})_3$. Substantial precipitation to palladium metal was observed with $P(o\text{-tol})_3$ and $P(OPh)_3$. A light yellow solution was obtained with PBu_3 which indicated formation of some stable complexes. $P(OPh)_3$ and PBu_3 selectively resulted in formation of the branched ester. PPh_3 gave the highest activity (TOF = 408 h^{-1}).

3.4.3 Effect of acid promoter

3.4.3.1 Effect of acid promoter concentration

Methanesulfonic acid was used as the acidic promoter. The molar ratio of methanesulfonic acid to palladium was varied at 90°C and 70 bar carbon monoxide pressure keeping the molar ratio of triphenylphosphine to palladium constant at 6 (see Table 3.12). It is reported that the presence of an acid is necessary to form the catalytically active cationic species as without the acid the reaction does not occur and $Pd(OAc)_2(PPh_3)_2$ is isolated from the reaction mixture [1,2]. The turnover frequency was found to increase up to a molar ratio of methanesulfonic acid to palladium of 35.

Table 3.12 : Effect of molar ratio of methanesulfonic acid to palladium on the turnover frequency (TOF, determined from the number of moles of CO converted during the initial 15 minutes) and selectivity in the 1-hexene hydroesterification after a reaction time of 60 minutes ($T_{reaction}$=90°C; p_{CO} = 70 bar; $n_{1\text{-hexene}}$=50 mmol; $n_{methanol}$=0.99 mol; n_{Pd}=0.56 mmol; Pd: PPh_3 = 1:6; stirring speed: 1000 rpm)

$n_{methanesulfonic\ acid}/n_{Pd}$ mol/mol	TOF hr^{-1}	$S_{2\text{-hexene}}$ mol-%	$S_{3\text{-hexene}}$ mol-%	S_{ester} mol-%	$C_{n\text{-ester}}$ mol-%	$C_{i\text{-ester}}$ mol-%	$C_{i'\text{-ester}}$ mol-%	n:i
6	40	67	11	22	45	45	10	1:1
23	210	18	3	79	63	31	6	2:1
35	213	39	8	54	62	32	6	1.9:1
46	102	45	11	44	48	44	8	1.1:1

The selectivity for the formation of esters is very low at low molar ratios of methanesulfonic acid to palladium. At a molar ratio of methanesulfonic acid to palladium of 23 the selectivity for the formation of esters is 79 mol-%. It decreases upon further increase of the molar ratio of methanesulfonic acid to palladium.

At low molar ratios there is not enough methanesulfonic acid present to form the catalytically active species hence the competing double-bond isomerisation takes place. With increasing methanesulfonic acid, the acid competes with the PPh_3 and reactant molecules for coordination causing a decrease in the activity.

3.4.3.2 Variation of the type of acid

The effect of different acidic promoters on catalytic activity was studied at base-case conditions using a molar ratio of palladium to triphenylphosphine to acid of 1:6:46 (see Table 3.13). No catalytic activity was observed in the presence of trifluoroacetic acid and chlorosulfonic acid. Using para-toluene sulfonic acid results in a higher activity and a higher selectivity for the formation of the esters. The distribution of the ester compounds is, however, only marginally affected.

Table 3.13 : Effect of acidic promoter on the turnover frequency (TOF, determined from the number of moles of CO converted during the initial 15 minutes) and selectivity in the 1-hexene hydroesterification after a reaction time of 60 minutes ($T_{reaction}$=90°C; p_{CO} = 70 bar; $n_{1\text{-hexene}}$=50 mmol; $n_{methanol}$=0.99 mol; n_{Pd}=0.56 mmol; Pd: PPh_3: acid = 1:6:46; stirring speed: 1000 rpm)

Promoter	TOF hr^{-1}	$S_{2\text{-hexene}}$ mol-%	$S_{3\text{-hexene}}$ mol-%	S_{ester} mol-%	$C_{n\text{-ester}}$ mol-%	$C_{i\text{-ester}}$ mol-%	$C_{i'\text{-ester}}$ mol-%	n:i
MSA[1]	102	45	11	44	48	44	8	1.1:1
p-TSA[2]	184	43	8	49	44	46	10	0.96:1

[1]MSA = methanesulfonic acid

[2]p-TSA = para-toluenesulfonic acid

4. Discussion

4.1 Catalyst system

The catalyst used in this study was generated in situ from a mixture of $Pd(OAc)_2$/ PPh_3/ MsOH. $Pd(OAc)_2$ reacts with PPh_3 forming a yellow complex, $Pd(OAc)_2PPh_3$ [1,2] which transforms mainly to $Pd(OMs)_2(PPh_3)_2$ (I) on subsequent reaction with methanesulfonic acid [1].

$$Pd(OAc)_2 + 2PPh_3 + 2MsOH \longrightarrow \underset{\mathbf{I}}{Pd(OMs)_2(PPh_3)_2} + 2\,AcOH \qquad \mathbf{(4.1)}$$

This catalytic system is reported to be significantly more active than the neutral precursor such as $PdCl_2(PPh_3)_2$ [44]. The charge of the central metal cation in $Pd(OMs)_2PPh_3$ is balanced by weakly coordinating anion OMs^- so that the metal cation has easily available coordination sites capable of activating the reactant molecules. These are more effective than the neutral system where the charge of the central metal cation is balanced by strongly coordinating anion Cl^- [46].

$$Pd(OAc)_2(PPh_3)_2 \xrightarrow{TsOH,\ CO} [HPd(PPh_3)_{n-z}(CO)_mL]^+TsO^- + 2HOAc \qquad \mathbf{(4.2)}$$

$$Pd(OAc)_2(PPh_3)_2 + TsOH + MeOH + CO \longrightarrow Pd(COOMe)(PPh_3)_2(TsO) + 2AcOH \qquad \mathbf{(4.3)}$$

where, $L = TsO^-$ or H_2O; $n = 1$ or 2; $m = 1$ or 2; $z = m-1$

The presence of methanesulfonic acid is necessary to form the catalytically active cationic species as without the sulfonic acid the reaction does not occur and $Pd(OAc)_2(PPh_3)_2$ complex was isolated from the final reaction mixture [46]. In the presence of excess PPh_3 and methanol, formation of the Pd-carbomethoxy complex, which is inactive or lower in activity is quite facile.

At base-case conditions, the TOF is constant in the initial 15 minutes whereupon it decreases significantly. This is a result of PPh_3, CO and

methanol competing for coordination with the reactant molecules thus decreasing the concentration of the active Pd-H species [32].

In the reaction, increasing levels of phosphonium sulfonate salts are formed [45]. The formation of these phosphonium salts leads to a decrease in free phosphine in the solution. This results in a decrease in the concentration of the catalytically active species hence a drop in activity. The decrease in TOF with reaction time (Fig. 3.1) might be attributed to depletion in phosphine concentration.

At high PPh_3 ratios, the ligand competes with the reactant molecules for coordination causing a decrease in activity. The product selectivity is affected drastically by the nature of the ligands [46]. At high ligand concentrations, the concentration of active species is strongly decreased which leads to inhibition of the catalytic process (eq. 1.3). With the increase in the PPh_3 concentration, it is likely that the palladium centre can have more than one PPh_3, which can increase the steric as well as the electronic density at the metal centre thus shifting the equilibrium towards linear product formation. Lower levels of double-bond isomers were observed at high ligand concentrations.

Tris(p-methoxyphenyl)phosphine gave better activity (TOF = 273 hr^{-1}) relative to PPh_3 and diphenyl-2-pyridylphosphine at a molar excess of 6 to Pd. Higher n:i ratios were obtained with the two bulky ligands. PPh_3 gave the highest activity (TOF = 408 hr^{-1}) and n:i ratio at a higher PPh_3 excess of 30. Olefin migration to coordinated CO can also be affected by the different electronic properties of the ligands. With the absence of substituents on the benzene ring, this behaviour may be attributed to the modified ability of the metal to co-ordinate the olefin and carbon monoxide. Coordination of the olefin would be disfavoured with the more basic ligands like the tris(p-methoxyphenyl)phosphine, because of its nucleophilic character, while with the less basic ligands, the olefin would bind strongly [46]. With both styrene [46] and 1-hexene, PPh_3 gave the highest activity.

In the absence of an acidic promoter, the Pd-hydride species may be formed by a reaction with methanol itself [46]. However, formation of the Pd metal or Pd(0) complex in the presence of PPh_3 might be due to reduction by the hydride (eq. 1.9) [31]. It is also very likely that the acid plays an important role in the reactivation of any Pd(0) that may form during the course of catalysis by regenerating the active Pd-H species (eq. 1.10) [47,48]. At lower concentrations of the acid and in the presence of excess methanol the palladium precursor can form an inactive or less active palladium carbomethoxy complex.

A significant increase in activity was observed upon addition of a sulfonic acid. On varying the sulfonic acid concentration, an increase in TOF up to a certain ratio of acid and remaining constant on further increase was observed with styrene [46], cyclohexene [31] and 1-hexene. A maximum TOF of ca. 202 hr^{-1} was obtained for both styrene [46] and 1-hexene at PPh_3: Pd ratios of 4 and 6 using TsOH (10:1) and MsOH (23:1) respectively. With the cyclohexene, the TOF increased from 20 hr^{-1} in the absence of TsOH to 850 hr^{-1} at TsOH:Pd of 10:1 [31]. For styrene, selectivity was not affected by the change in TsOH implying weak coordination of the acid to the metal centre [46]. Higher n:i ratios were observed at higher acid concentrations probably due to the steric cloud at high acid concentrations.

Higher activity was observed at low palladium concentrations suggesting that only a small fraction of the metal is used in the generation of the catalytically active complex. High concentration of palladium may lead to formation of complexes of higher nuclearity, which results in palladium precipitation. Low turnover frequencies obtained at high palladium concentrations might be related to the substantial amounts of palladium black observed for such reactions.

At lower methanol concentrations, (2.5-8 mol/litre), the catalytic activity was found to increase linearly. A similar observation was reported in the hydroesterification of styrene [46] and cyclohexene [31]. From equations 1.8-1.10, it is clear that under the reaction conditions, the fraction of palladium

that forms the active species depends mainly on the methanol concentration. At lower methanol concentrations, formation of the alkoxy species is reduced hence higher rates would be obtained.

If the rate-limiting step in the hydroesterification is proposed to be nucleophilic attack of methanol on the acyl complex, the rate of reaction will be lower at lower concentrations of methanol [46]. Above a ratio of 10, the reaction became inhibited by methanol. This could be expected at high methanol concentrations as it is highly likely that a part of the catalyst precursor forms the carbomethoxy complex (reaction 4.3) or the methanol competes for coordination. The polarity of the medium does not seem to have an effect on the ester distribution as no trends could be deduced on varying the methanol.

For both 1-hexene and cyclohexene [31], the reaction can be approximated to be first-order with respect to olefin concentration. Double-bond isomerisation is inhibited in 1-hexene, which leads to higher selectivities to ester at high substrate concentrations. The observed change in selectivity pattern can be explained on the basis of the polarity of the medium. For the carboxylation of the propene, it was reported that the reaction medium has a pronounced effect on the selectivity [49]. At higher concentrations of 1-hexene the medium is less polar which favours formation of the normal product hence higher n-to-i ratios due to enhanced coordination of cationic and anionic species.

CO strongly inhibits the reaction as shown by a strong decline in activity on increasing the CO pressure. At high carbon monoxide pressure, the CO molecules compete with the reactants for coordination thus resulting in a decrease in catalytic activity. To maintain good rates, reactions have to be performed at low CO pressures. The higher concentration of double-bond isomers at high CO pressures leads to a low linear ester content and lower n:i.

Above 110 °C, the catalyst partially decomposed to palladium black. The true dependency of the reaction rate on temperature may not be accurately estimated due to decomposition of the active species as the temperature is

increased. Lower concentration of double-bond isomers was observed at high temperatures resulting in enhanced ester formation.

4.2 Reaction kinetics

4.2.1 Mechanistic and kinetic preview

The proposed cycles for hydroesterification reactions entail the hydride and the carbomethoxy mechanism [32].

$$[Pd\text{-}H]^+ \overset{c=c}{\rightleftharpoons} [Pd\text{-}C\text{-}CO\text{-}H]^+ \overset{CO}{\rightleftharpoons} [Pd\text{-}CO\text{-}C\text{-}C\text{-}H]^+ \xrightarrow{ROH} [Pd\text{-}H] + H\text{-}C\text{-}C\text{-}COOR \qquad \textbf{(4.4)}$$

$$[Pd\text{-}CO\text{-}OR]^+ \overset{C=C}{\rightleftharpoons} [Pd\text{-}C\text{-}C\text{-}CO\text{-}OR]^+ \xrightarrow{CO,\ ROH} [Pd\text{-}CO\text{-}OR]^+ + H\text{-}C\text{-}C\text{-}COOR \qquad \textbf{(4.5)}$$

It is very likely that both pathways are operating simultaneously, since formation of palladium-carbomethoxy complexes is quite facile in methanol as a solvent and that of palladium-hydride is favoured by the presence of acidic promoters. It was shown that the carbomethoxy complex is prone to decompose to inactive Pd(0) complexes leading to a lower activity [36].

The hydride mechanism starts from a Pd-H species. The promoting effect of methanesulfonic acid is discussed in terms of favouring the formation of a Pd-H species, which initiates the catalytic cycle [32]. The sulfonic acid would favour the formation of a Pd-H species by reactivating any Pd(0) species that may form during the course of catalysis. On the basis of the promoting effect of a hydride source such as methanesulfonic acid, it is likely that the palladium-hydride mechanism plays a major role.

In the range of concentration studied, the reaction rate of CO consumption is approximated to be first-order with respect to 1-hexene with a first-order rate constant of 89 litre/(mol Pd.hr). Kinetic inhibition was observed at high concentrations of CO, methanol, Pd and PPh_3. The role of PPh_3 was ignored in the model due to the probable loss by decomposition or as phosphonium salts [45], which was not quantified. The side reactions leading to phosphine consumption leads to Pd-black thus making it difficult to distinguish between the effect of Pd and PPh_3 on catalytic activity.

5. CONCLUSIONS

The hydroesterification of 1-hexene is catalysed by a $Pd(OAc)_2$/ PPh_3/MsOH catalyst system in methanol as solvent. The active catalyst system is formed *in situ*. The main competing reaction is isomerisation of the 1-hexene to 2-hexene and 3-hexene. Formation of methyl-2-ethylpentanoate was observed which suggested hydroesterification of the internal olefins. The double-bond isomerisation is not affected as strongly as the hydroesterification by the partial pressure of carbon monoxide.

The reaction can be approximated to be first-order with respect to 1-hexene concentration (1.25-3.13 mol/litre). Carbon monoxide and palladium concentrations strongly inhibit the hydroesterification of 1-hexene. The reaction rate increased up to a methanol concentration of 8 mol/litre, PPh_3 excess of 30 to palladium and a methanesulfonic acid excess of 23 to palladium. Inhibition was observed at higher concentrations of methanol, PPh_3 and methanesulfonic acid. However, there is a need for a large excess of the ligand and acid promoter for the formation of the catalytically active species. In the temperature range between 50 and 90°C, activation energy of 30 kJ/mol was determined.

6. REFERENCES

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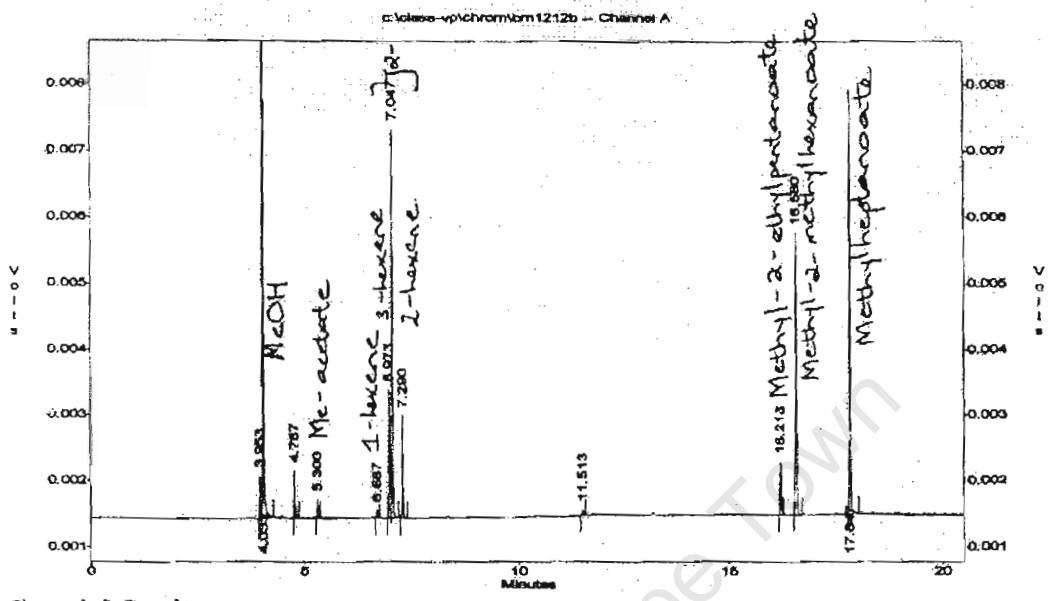
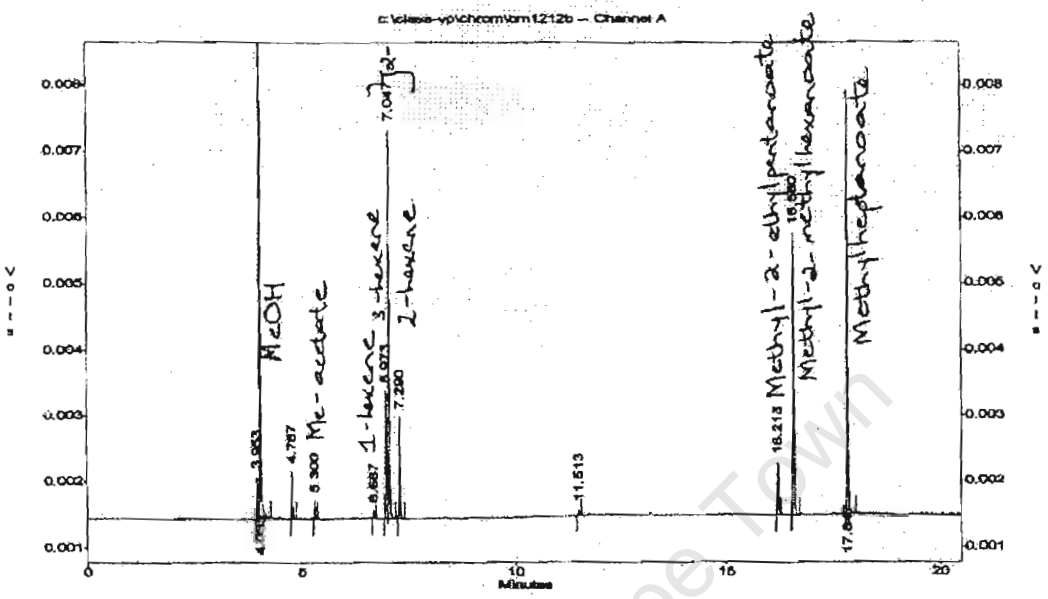


Channel A Results

Peak	Time	Area	Area %
1	3.95	651	0.357
2	4.03	140423	76.909
3	4.77	952	0.521
4	5.30	401	0.220
5	6.69	207	0.113
6	6.97	3293	1.804
7	7.05	10456	5.727
8	7.29	2689	1.473
9	11.51	242	0.133
10	16.21	1639	0.898
11	16.58	8584	4.701
12	17.85	13047	7.146
Totals :		182584	100.000

A1 Gas Chromatogram of a typical base-case reaction



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